ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF ACRYLIC ACID-MALEIC ANHYDRIDE COPOLYMERS AND THEIR USE IN WATER BORNE PAINTS

M.Sc. THESIS

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Department of Polymer Science and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

AKRİLİK ASİT – MALEİK ANHİDRİT KOPOLİMERLERİNİN SENTEZİ, KARAKTERİZASYONU VE SU BAZLI BOYALARDA KULLANIMI

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HAZİRAN 2014

Bahadır KAYA, a **M.Sc.** student of ITU **Institute of Science and Technology/ Graduate School of Istanbul Technical University** student ID 515111002, successfully defended the **thesis** entitled "**Synthesis and Characterization of Acrylic Acid-Maleic Anhydride Copolymers and Their Use In Water Borne Paints** ", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. İ. Ersin SERHATLI** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. Ayşen ÖNEN** İstanbul Technical University	.....
	Prof. Dr. Yusuf Menceloğlu Sabancı University	.....

Date of Submission: 5 May 2014
Date of Defense: 29 May 2014

To my family,

FOREWORD

I would firstly like to express my deep appreciation and thanks for my supervisor Prof. Dr. İ. Ersin SERHATLI for his support, humanity, kindliness, encouragement throughout the whole study and for providing me to study of master degree at Istanbul Technical University.

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June 2014

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Chemical Engineer

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ABBREVIATIONS

PAA : Polyacrylic Acids
P(AA-MA) : Copolymers of Acrylic-Maleic Anhydride
NaPAA : Sodium Salts of Polyacrylic Acid
NaP(AA-MA) : **S**odium Salts of Acrylic-Maleic Anhydride Copolymers
RAFT : Reversible Addition Fragmentation Chain Transfer
AA : Acrylic Acid
MA : Maleic Anhydride
FTIR : Fourier Transform Infrared Spectroscopy
GPC : Gel Permeation Chromatography
RALS : Right Angle Light Scattering
LALS : Left Angle Light Scattering
RI : Refractive Index
UV : Ultra Violet
HEC : Hexa Ethyl Cellulose
MEG : Mono Ethylene Glycol
KU : Krebs Units
cP : Centipoise
gm : Grams
ASTM : American Society for Testing and Materials
∆E : Color Difference
IEP : Isoelectric Point
PDI : Polydispersity Index
NMP : Nitroxide Mediated Polymerization
ATRP : Atom Transfer Radical Polymerization
APS : Ammonium Persulfate
NaHyp : Sodium Hypophosphite
NaOH : Sodium Hydroxide
IPA : Isopropyl Alcohol
HPLC : High Performance Liquid Chromatography
PBS : Phosphate Buffered Saline
cP : Centipoise
gm : Grams
nm : Nanometer
mV : Mill Volt
NMR : Nuclear Magnetic Resonance

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SYNTHESIS AND CHARACTERIZATION OF ACRYLIC ACID-MALEIC ANHYDRIDE COPOLYMERS AND THEIR USE IN WATER BORNE PAINTS

SUMMARY

The paint emerges in every area of our colorful life. The usage areas of paint are expanding and the consumption of it is gradually increasing nowadays. The paint is applied on the surface of a thin film on the surface layer which provides protection against external factors, in addition to the surface in a decorative feature gives a chemical coating.

A paint formulation is made up with a mixture of several materials. Basically, the four main elements are present in the structure of paint. These are binders, pigments, additives and solvents. Rates of usage these materials is a different type of paint to change. Pigments, insoluble organic and inorganic substances, are giving color, hiding power and protective properties to paint. Color pigments are used in order to give them color and fillers are used in order to filling power and cost reduction them. The filler may form 20 to 50% of the paint. The usage purposes of these substances in paint formulation, to control rheological properties, to reduce brightness, to increase the mechanical properties of the paint film or to develop film barrier properties of the paint. Titanium dioxide, iron oxide, zinc oxide, zinc phosphate is given as examples pigments and titanium dioxide is the most widely used in paint pigments. Calcite, calcium and barium compounds, dolomite, gypsum, talc and limestone, are examples of the fillers. Calcite is the most widely used in paint as fillers. Turkey's paint total industrial production is taken as a basis Europe's 6th largest paint manufacturer but imported raw materials and the rate of approximately 65 %, while Turkey and paint industries dependent on outside. Considering the increase in the production in the raw material dependence is increasing day by day.

The most common type polyelectrolyte are used as dispersing agent for obtaining stable dispersion of water borne paint formulations. They are divided into inorganic and organic polyelectrolytes. Organic polyelectrolyte dispersing additives are relatively low molecular weight polymers. Polyacrylic acids (PAA) and copolymers of acrylic-maleic anhydride P(AA-MA) are examples of organic polyelectrolytes. Polyacrylic acid and its derivatives are used in disposable diapers, ion exchange resins, coatings and a thickening, dispersing, suspending and emulsifying agents in pharmaceutical, cosmetic and paint industrials. The most commonly used dispersants in paint industry with molecular weights of 1,000 and 20,000 g/mol ranging PAA and P(AA-MA) derivatives. These polymers are provided with water solubility by ammonium, sodium or potassium hydroxide neutralization. Sodium salts of polyacrylic acid (NaPAA) are most used dispersant agent in water borne paint formulations.

In this study, stabilization of water borne paint formulations was examined by using NaPAA and sodium salts of copolymers of acrylic-maleic anhydride NaP(AA-MA)

as dispersant agents. PAA was synthesized from controlled radical polymerization of acrylic acid via reversible addition-fragmentation chain transfer (RAFT) method and P(AA-MA) was synthesized from controlled radical copolymerization of acrylic acid and maleic anhydride via same method. NaPAA and NaP(AA-MA) were obtained from neutralization of PAA and P(AA-MA) with sodium hydroxide (32% wt.).

In order to determine optimal polymerization parameters, NaPAA was synthesized in four different ways which were changing amount of chain transfer agent, sodium hypophosphite, changing ratio of initiator and monomer, changing feeding time of monomer and changing amount of solvent, isopropyl alcohol.

Moreover, in order to determine desirable acrylic acid-maleic anhydride monomers ratio, NaP(AA-MA) was synthesized in AA/MA: 1:1 and 1:0.5 ratios. Additionally, the AA/MA: 0.5:1 ratio was tried to synthesis but the product crystallized at room temperature due to crystallization tendency of the highly amount of maleic anhydride at room temperature.

The synthesized samples were structurally identified by performing the Fourier transform infrared spectroscopy (FTIR) characterization. FTIR spectrum gives the peaks that are expected due to the chemical structure of PAA, NaPAA, P(AA-MA) and Na(AA-MA). The solid content of polymers was determined by rapid solid content analyzer. The Brookfield viscosity of polymers was measured at 6 rpm at 20°C. Molecular weight and molecular weight distribution were determined via GPC equipped tetra detection of RALS and LALS, RI, UV and viscometer detectors.

In order to determine dispersion efficiency, the mineral solid content of slurry was 66 weight of percent 5 micron $CaCO_3$ was prepared. Then, the slurry and synthesized NaPAA or NaP(AA-MA) dispersant agents were mixed together in a dispersion bowl until the slurry became homogeneous for 20 minutes at 2000 rpm with mechanical mixer. The viscosity of calcite slurries was measured using a low shear viscometer Brookfield Model DV-II at 60 rpm and 20°C in order to determine dispersion efficiency of synthesized NaPAA polymers and NaP(AA-MA) copolymers. The viscosity of calcite slurries was then recorded at 20°C and varied amount of NaPAA and NaP(AA-MA) were added again for creating the curve of viscosity versus NaPAA and NaP(AA-MA) dispersant agents concentration.

The zeta potential of calcite slurries added varying amount of NaPAA or NaP(AA-MA) as a dispersant was measured with zeta potential meter in order to examine stabilization of calcite slurries.

Then, a sample formulation of water borne white plastic paint that has 74 PVC value and prepared with synthesized NaPAA polymers or NaP(AA-MA) copolymers as a dispersing agent was chosen in order to examine the performance of waterborne paint formulations. The grindometer measurement of paint formulations was realized for confirming fineness of dispersion and detecting of oversize particles in paint dispersion. The paint films were applied to hiding power cards. In the next step, the luminous Y-reflectance the darker and the lighter area of it were measured with a spectrophotometer for calculating opacity value of prepared paint formulations. The initial viscosity of paint formulations was measured using a low shear viscometer Brookfield Model DV-II with in order to determine dispersion and stabilization efficiency of synthesized NaPAA polymers and NaP(AA-MA) copolymers in paints.

The rheological stability changes of the prepared paint formulations over time and under temperature was determined by measuring the Brookfield viscosities of the

different paint formulations at 1 rpm with spindle s-64 at 20°C, after storage one week for one month at 52±1°C. The storage viscosity measurements can explain as; the dispersion efficiency of it on paint formulations improved when molecular weight and molecular distribution of polymeric dispersant agent decreased. In order to easily obtain low molecular weight and narrow molecular weight distribution NaPAA, sodium hypophosphite can be used as chain regulator in isopropyl alcohol and water media. In addition, the feeding time of monomer and initiator influences on molecular weight and narrow molecular weight distribution of NaPAA. When the feeding time was increased, molecular weight was decreased and molecular weight distribution was narrowed. Moreover, NaP(AA-MA) that was synthesized in 1:0.5 AA/MA monomer ratio can be used as dispersing agent in water borne paint formulations, instead of NaPAA polymers to present good storage stability performance in paints.

AKRİLİK ASİT – MALEİK ANHİDRİT KOPOLİMERLERİNİN SENTEZİ, KARAKTERİZASYONU VE SU BAZLI BOYALARDA KULLANIMI

ÖZET

Boya renkli hayatımızın her alanında karşımıza çıkar. Günümüzde, kullanım alanları genişlemekte ve tüketimi giderek artmaktadır. Boya uygulandığı yüzey üzerinde ince bir film tabakası oluşturarak, yüzeyin dış etkenlere karşı korunmasını sağlayan, bunun yanında yüzeye dekoratif bir özellik kazandıran kimyasal bir kaplama malzemesidir.

Bir boya formülasyonu bir kaç malzemenin karışımı ile oluşmaktadır. Temel olarak, boyanın yapısında dört ana unsur bulunmaktadır. Bunlar; bağlayıcılar, pigmentler, katkı maddeleri ve çözücülerdir. Bu malzemelerin kullanım oranları farklı tip boyalar için değişiklik göstermektedir. Pigmentler boyaya renk, örtücülük ve koruyuculuk kazandıran organik ve inorganik maddelerdir. Pigmentler herhangi bir çözeltide çözünmeyen maddelerdir. Renk vermek amacıyla kullanılanlara renk pigmenti, dolgu gücü ve maliyet düşürme amacıyla kullanılanlara dolgu maddeleri adı verilir. Dolgu maddeleri boyaların %20-50'sini oluşturabilmektedir. Bu maddeler reolojik özellikleri kontrol etme, parlaklığı azaltma, mekanik özellikleri arttırma ya da boya filminin bariyer özelliklerini geliştirme amacıyla boya formülasyonlarında kullanılır. Titanyum dioksit, demir oksit, çinko oksit, çinko fosfat yaygın olarak kullanılan pigmentlere örnek gösterilebilir. Titanyum dioksit boyada kullanılan en yaygın pigmenttir. Kalsiyum ve baryum bileşikleri, kalsit, dolomit, alçıtaşı, talk ve kireçtaşı ise dolgu maddelerine örnek olarak verilebilir. Kalsit boyada kullanılan en yaygın dolgu maddesidir. Türkiye boya sanayi toplam üretim esas alındığında Avrupa' nın 6. büyük boya üreticidir. İthal hammadde oranı yaklaşık olarak %65' i bulurken, Türkiye boya sanayi dışa bağımlı durumdadır. Üretim artışı göz önünde bulundurulduğunda hammaddedeki dışa bağımlılık gün geçtikçe artmaktadır.

Su bazlı boyalarda inorganik pigmentler için kullanılan en genel tip dispersiyon katkısı polielektrolitlerdir. Bunlar inorganik ve organik polielektrolitler olarak ikiye ayrılır. Organik polielektrolit dispersiyon katkıları, nispeten düşük molekül ağırlıklı polimerlerdir. Organik polielektrolitlere poliakrilik asitler (PAA) ve akrilik-maleik anhidrit P(AA-MA) kopolimerler örnek gösterilebilir. Poliakrilik asitler ve bunların türevleri tek kullanımlık çocuk bezlerinde, iyon değiştirme reçinelerinde, kaplamalarda, kalınlaştırıcı, dağıtıcı, süspanse edici ve emülsifiye edici maddeler olarak ise; ilaç, kozmetik ve boya endüstrilerinde kullanılır. Boya sektöründe dispersant olarak en yaygın kullanılan, molekül ağırlıkları 1.000 ve 20.000 g/mol arasında PAA ve P(AA-MA) türevleridir. Bu maddeler amonyum, sodyum veya potasyum hidroksit ile nötralize edilerek suda çözünürlükleri sağlanır. Poliakrilik asidin sodyum tuzu (NaPAA) su bazlı boya formulasyonlarında en çok kullanılan dispersant ajanıdır.

PAA genellikle serbest radikalik polimerizasyon yöntemi ile üretilmektedir. Birkaç binden birkaç yüz bin molekül ağırlığına sahip polimerler elde edilebilmektedir. Boya sektöründe en yaygın dispersant olarak kullanılan PAA'ların molekül ağırlıkları 1.000 ve 20.000 g/mol arasındadır. Molekül ağırlığı başlatıcı ve zincir transfer ajanı miktarı ayarlanarak kontrol edilebilmektedir. Kontrollü radikal polimerizasyonunun; nitroksit aracılıklı polimerizasyon (NMP), atom transfer radikal polimerizasyonu (ATRP) ve tersinir eklenme-parçalanma zincir transferi (RAFT) olmak üzere üç farklı tipi vardır.

Akrilik asidin NMP polimerizasyonu ile eldesinde, nitroksidin asidik ortamda degredasyon problemi söz konusudur. Akrilik asidin atom transfer radikal polimerizasyonunda ise polimere metal tutunması kontrol edilememektedir. Bu nedenle, düşük molekül ağırlığına ve düşük PDI değerine sahip poliakrilik asit üretilebilmesi için en uygun yöntem tersinir eklenme-parçalanma zincir transferi (RAFT) yöntemidir.

Bu çalışmada, NaPAA ve akrilik-maleik anhidrit kopolimeri sodyum tuzunun (NaP(AA-MA)) dispersant olarak kullanıldığı su bazlı boya formulasyonlarının stabilizasyonu üzerinde çalışılmıştır. PAA, akrilik asidin "Tersinir eklenme-parçalanma zincir transferi" metodu ile kontrollü radikal polimerizasyonundan ve P(AA-MA), akrilik ve maleik anhidritin aynı metod ile kontrollü radikal kopolimerizasyonundan sentezlenmiştir. NaPAA ve NaP(AA-MA), PAA ve P(AA-MA)'nın sodyum hidroksit (ağırlıkça %32'lik) ile nötralizasyonundan elde edilmiştir.

NaPAA, en uygun polimerizasyon parametrelerini belirlemek için; değişen miktarda zincir transfer ajanı miktarının değiştirilmesi, başlatıcı ve monomer oranının değiştirilmesi, monomer ve başlatıcının besleme süresinin değiştirilmesi ve çözücü miktarının değiştirilmesi ile dört farklı yoldan sentezlenmiştir.

Ayrıca, istenilen akrilik asit-maleik anhidrit monomer oranının belirlenmesi için AA/MA: 1:1 ve AA/MA: 1:0.5 oranlarında sentezlenmiştir. Ek olarak, AA/MA: 0.5:1 oranı sentezlenmeye çalışılmış ancak yüksek miktarda maleik anhidritin oda sıcaklığında kristalleşme eğilimi nedeniyle ürün kristalleşmiştir.

Sentezlenen numuneler yapısal olarak FTIR ile tespit edilmiştir. FTIR spektrumu PAA, NaPAA, P(AA-MA) ve Na(AA-MA)'nın kimyasal yapısı gereği beklenen pikleri vermiştir. Sentezlenen polimerlerin katı içerikleri hızlı katı ölçer cihazı ile belirlenmiştir. Polimerlerin Brookfield viskoziteleri 6 rpm de 20°C de ölçülmüştür. Molekül ağırlığı ve moleküler ağırlık dağılımları 4'lü RALS ve LALS, RI, UV ve viskozimetre detektörlü GPC ile saptanmıştır.

Sentezlenen PAA' lardaki polimerizasyona girmemiş akrilik asit monomeri miktarı HPLC ile belirlenmiştir. Akrilik asidin yüzde dönüşümü polimerizasyona girmemiş akrilik asit monomer miktarı yardımıyla hesaplanmıştır. Hesaplanan akrilik asidin yüzde dönüşümlerine göre; zincir düzenleyici ajan olarak kullanılan NaHyp ve kullanılan çözümü miktarları arttıkça dönüşüm artmaktadır. APS/AA oranı % 5, 6 ve 7.5 olduğunda %94'ün üzerinde monomer dönüşümü elde edilebilmektedir. Başlatıcı besleme süresi 4.5 saatten 5.5 saate çıkarıldığında monomer döüşümü neredeyse aynı kalmış olup başlatıcı besleme süresi 6.5 saat olduğunda %98.72 ile en yüksek monomer dönüşümü sağlanabilmiştir.

Sentezlenen NaP(AA-MA) kopolimerlerinin akrilik asit ve maleik anhidrit monomer oranlarını belirleyebilmek için ^{1}H-NMR analizleri yapılmıştır. Mikrodalga fırında kurutulan kopolimer örnekleri, dötero suda çözülerek NMR cihazına verilmiştir.

C1_Na kopolimerinin teorik maleik anhidrit monomer oranı %33 olmasına rağmen, elde edilen ^{1}H-NMR analiz sonuçlarına göre; AA/MA monomer oranı 1:0.5 olan C1_Na kopolimerinde maleik anhidrit monomer oranı %23 ve akrilik asit monomer oranı %77 dir. Ayrıca, sentezlenen bir diğer kopolimer olan C2_Na kopolimerinin teorik maleik anhidrit monomer oranı %50 olmasına rağmen, ^{1}H-NMR analiz sonuçlarına göre; AA/MA monomer oranı 1:1 olan C2_Na kopolimerinde maleik anhidrit monomer oranı %38 ve akrilik asit monomer oranı %62 dir. Teorik ve gerçekleşen monomer oranları arasındaki bu farklılığın nedeni ise sterik engellemedir. Maleik anhidrit sulu ortamdaki kopolimerizasyona çok az eğilim sergiler. Kopolimerizasyonun yayılma basamağında monomer molekülü yayılan radikal grup tarafından sterik olarak engellenir. Böylece, kopolimerizasyonun yayılma basamağı son derece yavaş gerçekleşir.

Dispersiyon etkinliğini belirlemek için katı içeriği %66'lık 5 mikronluk kalsiyum karbonat içeren sulu karışım hazırlanmıştır. Daha sonra, sulu karışım ve sentezlenen NaPAA ya da NaP(AA-MA) dispersiyon ajanları bir dispersiyon kabına konularak homojen karışım oluşturuncaya kadar mekanik karıştırıcı ile 2000 rpm de 20 dakika süre ile karıştırılmıştır. NaPAA polimerlerinin ve NaP(AA-MA) kopolimerlerinin dispersiyon etkinliklerini belirlemek için kalsit sulu karışımlarının viskoziteleri 60 rpm de 20°C de bir Brookfield DV-II model viskozimetre ile ölçülmüştür. Kalsit sulu karışımlarının viskozitelerine karşılık değişen miktarlarda NaPAA ve NaP(AA-MA) dispersiyon ajanı içeren eğimi oluşturmak için viskoziteler kaydedilmiştir.

Dispersiyon ajanı olarak değişen miktarlarda NaPAA ya da NaP(AA-MA) eklenmiş kalsit sulu karışımlarının stabilizasyonunu incelemek için bir zeta potansiyeli ölçer ile sulu karışımların zeta potansiyeli ölçülmüştür.

Daha sonra, su bazlı boya formülasyonlarının performanslarını incelemek için 74 PVC değerine sahip ve dispersiyon ajanı olarak NaPAA polimerleri ya da NaP(AA-MA) kopolimerleri ile hazırlanmış örnek bir su bazlı plastik boya formulasyonu seçilmiştir. Boya formülasyonlarının grindometre ölçümleri dispersiyonun inceliğini doğrulayan ve boya dispersiyonu içinde büyük boy parçacıkların saptanması için gerçekleştirilmiştir. Boya filmleri kapatıcılık kartlarına uygulanmıştır. Bir sonraki adımda; hazırlanan boyaların kapatıcılıklarının hesaplanması için kartların siyah ve beyaz alanlarının ışık yansıma şiddetleri bir spektrofotometre ile ölçülmüştür. Sentezlenen NaPAA polimerlerinin ve NaP(AA-MA) kopolimerlerinin boyadaki dispersiyon ve stabilizasyon etkinliklerini belirlemek için boya formulasyonlarının ilk viskoziteleri bir Brookfield DV-II model viskozimetre ile ölçülmüştür.

Hazırlanan boya formulasyonlarının zamanla ve sıcaklık altında reolojik stabilitelerindeki değişimler 52±1°C de bir ay depolanıp bir hafta arayla Brookfield viskozitelerinin 20°C'de ölçülmesi ile belirlenmiştir. Depolama viskozitelerinin ölçümü polimerik dispersiyon ajanının molekül ağırlığı ve molekül dağılımı azaldıkça boya formulasyonlarının dispersiyon etkinliğini geliştirdiğini açıklamaktadır. Düşük bir moleküler ağırlığa ve dar bir molekül ağırlığı dağılımına sahip NaPAA kolaylıkla elde etmek için sodyum hipofosfit zincir düzenleyici olarak izopropil alkol ve su karışımı içerisinde kullanılabilir. Ek olarak, monomer ve başlatıcının besleme süresi NaPAA'nın molekül ağırlığı ve molekül ağırlığı dağılımını etkilemektedir. Besleme zamanı arttığında, molekül ağırlığı azalmış ve molekül ağırlığı dağılımı daraltılmıştır. Ayrıca, 1:0.5 AA/MA monomer oranına sahip NaP(AA-MA), su bazlı boya formulasyonlarında NaPAA yerine dispersiyon ajanı olarak kullanıldığında daha iyi depolama stabilite performansı sunmaktadır.

1. INTRODUCTION

The paint is applied on the surface of a thin film on the surface layer which provides protection against external factors, in addition to the surface in a decorative feature gives a chemical coating [1].

Turkey's paint total industrial production is taken as a basis Europe's 6th largest paint manufacturer. Production capacity of 800 thousand tons a year and is used to exist in the capacity of 65%. Water-based paints 55% of this capacity and 45% of the solvent-based paints constitute. According to these ratios, in Turkey, the year of about 285 thousand tons of water-based paint is produced. According to the different areas, the share of paint consumption in Turkey; construction paints 55%, wood furniture paints 15 %, marine paints 3%, automotive paints 9%, metal coatings 9%, powder coatings 7% and others 2 %. Domestic paint industry 20 of the upcoming large-scale and 600 close to the medium and small-scale enterprise is located. Imported raw materials and the rate of approximately 65 %, while Turkey and paint industries dependent on outside. Considering the increase in the production in the raw material dependence is increasing day by day [2].

The four main elements are present in the structure of paint. These are binders, pigments, additives and solvents. Rates of usage these materials is a different type of paint to change. Pigments, insoluble organic and inorganic substances, are giving color, hiding power and protective properties to paint. Color pigments are used in order to give them color and fillers are used in order to filling power and cost reduction them. The filler may form 20 to 50% of the paint. The usage purposes of these substances in paint formulation, to control rheological properties, to reduce brightness, to increase the mechanical properties of the paint film or to develop film barrier properties of the paint. Titanium dioxide, iron oxide, zinc oxide, zinc phosphate is given as examples pigments and titanium dioxide is the most widely used in paint pigments. Calcite, calcium and barium compounds, dolomite, gypsum, talc and limestone, are examples of the fillers. [1; 3; 4]

In order to obtain stable dispersion of water borne paint formulations, the most common type polyelectrolyte are used as dispersing agent. They are divided into inorganic and organic polyelectrolytes. Inorganic polyelectrolytes are polymeric phosphates. Polyphosphates can be degraded hydrolysis in 8-9 pH environments or creating strong complex with transition metals in environment. It decays can lead to unexpected changes in paint rheology.

Organic polyelectrolyte dispersing additives are relatively low molecular weight polymers. Polyacrylic acids (PAA) and copolymers of acrylic-maleic anhydride P(AA-MA) are examples of organic polyelectrolytes [3]. The most commonly used dispersants in paint systems with molecular weights of 1,000 and 20,000 g/mol ranging PAA and P(AA-MA) derivatives. These polymers are provided with water solubility by ammonium, sodium or potassium hydroxide neutralization. Sodium salts of polyacrylic acid (NaPAA) are most used dispersant agent in water borne paint formulations [5].

In this study, stabilization of water borne paint formulations was examined by using NaPAA and sodium salts of acrylic-maleic anhydride copolymers NaP(AA-MA) as dispersant agents. PAA and P(AA-MA) were synthesized from controlled radical polymerization of acrylic acid with reversible addition-fragmentation chain transfer (RAFT) method. NaPAA and NaP(AA-MA) were obtained neutralization of PAA with sodium hydroxide (32% wt.).

In order to determine optimal polymerization parameters, NaPAA was synthesized in four different ways which were varying amount of chain transfer agent, sodium hypophosphite, (0.05 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt%), ratio of initiator and monomer (ammonium persulfate/acrylic acid %: 2.5%, 5%, 6% and 7.5%), feeding time of monomer (4.5, 5.5 and 6.5 hours) and amount of solvent, isopropyl alcohol, (5 wt% and 10 wt%).

In order to determine acrylic acid-maleic anhydride monomers ratio, NaP(AA-MA) was synthesized in AA/MA: 1:1 and 1:0.5 ratio. Additionally, the AA/MA: 0.5:1 ratio was synthesized but the product crystallized at room temperature due to crystallization tendency of the highly amount of maleic anhydride at room temperature.

2. THEORETICAL PART

2.1 Paint Production

Paint production is a mixing process. First stage is called dispersing formulation or mill-base, the process of pigments distributed physical means. The subsequent steps of mill-base; binding and with the participation of certain additives "let down", mixing, testing and specification set is a step. Pigments and fillers typically are supplied in dry powder form. Although the primary particles are small in size, these particles are clustered together in the drying process forms lumps or agglomerates. Therefore, particles and fillers required to be dispersed into the liquid resin. In paint formulations, clumping, reduced brightness, pigments flotation, air bubble formation on the film surface, collapse pigments and rheology problems can be prevented with a good dispersion [6].

Wetting and dispersing additives are mixed to obtain well dispersed water borne paint formulations. During the mill base process, entrained air and adsorbed water on pigment and filler surface could be wetting with binder. In order to the interfacial tension difference between pigment and binder solution, dispersing and wetting additives are appropriately added in paint formulations.

The stages of mill base process is pictured in Figure 2.1 :. The mechanical energy disperse agglomerates of pigments and fillers by this way the particle size of them are decreased. In order to success of the dispersion process the technology of the dispersing equipment are continuous improved. The dispersed particles begin to reach a higher energy state than the starting agglomerates with applied mechanical energy. Due to the dispersed particles steadily attempt to reach their lowest energy state, the dispersed particles try to flocculate or agglomerate and break the stabilization. In addition, insufficiently stabilized pigmented coating systems will cause sedimentation, a decrease of gloss, a shift of color when rubbed, possible flooding and floating. The attached dispersion agent on the pigment surface prevents flocculation and sedimentation [6].

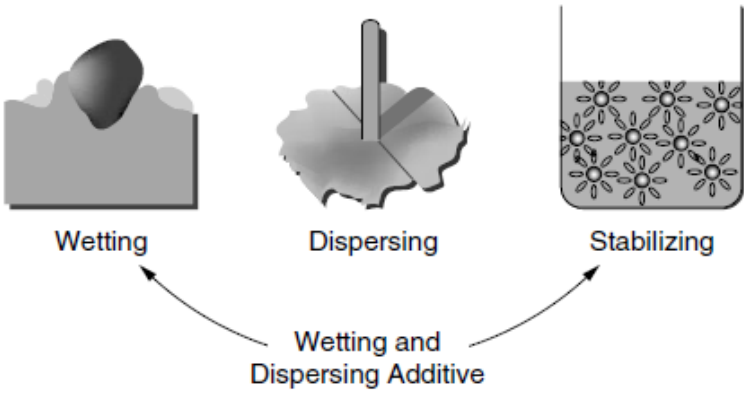


Figure 2.1 : The stages of mill base process [6].

2.2 Pigment Volume Concentration

The amount of binder in a paint formulation as compared to how much to use of pigments and fillers is important and affects the general properties of the paint. With binders in the paint formulation, the ratio of the total amount of pigments and fillers "Pigment Volume Concentration" (PVC) is called and PVC formula is calculated by equation.

$$PVC = \frac{(\text{Volume of the pigment})}{(\text{Volume of pigment} + \text{Volume of solid binder})} \times 100 \qquad \textbf{(2.1)}$$

According to this equation, if the PVC value of a paint formulation is 30, the total amount of pigments and fillers is 30% of the total paint formulation, the amount of binder is 70% of the total paint formulation. Pigments and fillers can be coated with binder amount should be a certain amount, and this amount "critical pigment volume concentration" is called [7].

The composition of modern water borne paints strongly depends on the desired application properties and therefore on the PVC. Typical mixture of a low PVC high gloss varnish contrast to a high PVC indoor paint is shown in Figure 2.2 :. In general, paints consist of water, a polymeric binder, pigments and filler particles. Additionally, additives like coalescents, thickeners, defoamers and dispersants are added to enable a sufficient stability and good application properties [6].

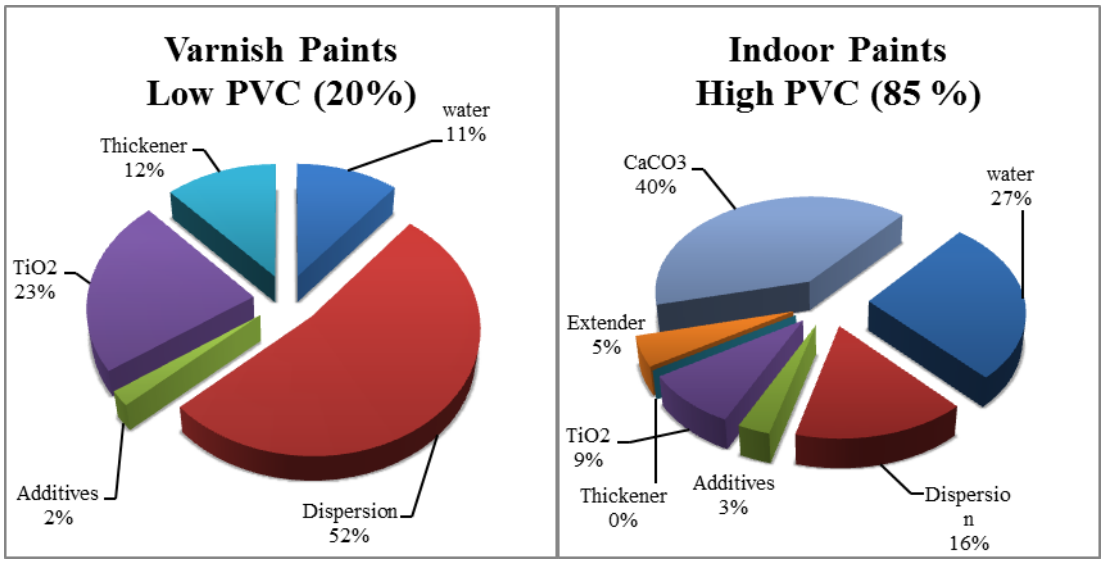


Figure 2.2 : Low PVC high gloss varnish contrast to a high PVC indoor paint [8].

The effects of PVC on paint film are observed in Figure 2.3 : values in a change of paints with different properties can be obtained. As an example, a very bright paint pigments and fillers that contain PVC value is zero. If matt paints contains a high amount of pigments and fillers and high PVC value of 55% to 80% are attained. PVC value of the primer is between 30% and 50% are semi-gloss and satin paint. Brightly colored paints have about 3% to 20% PVC value depending on the paint color. Generally, dark-colored gloss paints have lower PVC value [9].

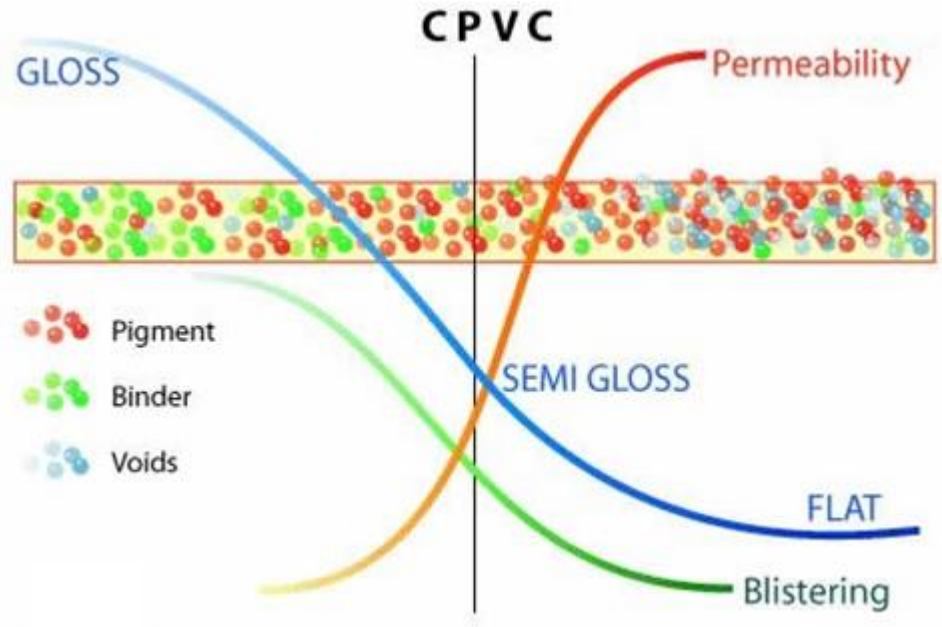


Figure 2.3 : The Effect of Pigment Volume Concentration on Paint Film [9].

2.2.1 Examples of water borne paint formulations

In Table 2.1 : water borne white ceiling, plastic and silk-matte paint formulations are illustrated. High filler containing pigment and water-based paints because they are more cost-effective often are used as ceiling paint. A high rate of PVC (PVC = 93) with a ceiling paint formulation examples are available in the following table. Binder ratio is high and called plastic paint and PVC ratio of 74, and PVC rate of 41 used as wall paint and the exemplary called silk-matt water-based paint formulation are presented in the following table. As shown in the example of water borne paint formulations, the dispersing agent usage amount varies with in different end-use water based paints.

Table 2.1 : Water Borne Paint Formulations [10].

Raw Materials of Water Borne Paint Formulations (wt. %)	**Water Borne White Ceiling Paint (PVC=93)**	**Water Borne White Plastic Paint (PVC=74)**	**Water Borne Silk-Matte Paint Formulation (PVC=41)**
Titanium Dioxide	4.00	12.00	20.00
Calcium Carbonate (Calcite)	62.30	38.40	13.90
Talk	0.00	3.00	4.00
Kaolin	1.00	4.00	3.00
Acrylic Binders	4.00	15.00	39.00
Sodium hexametaphosphate (Calgon)	0.10	0.10	0.10
Hexa ethyl cellulose (HEC)	0.45	0.40	0.30
Sodium Hydroxide	0.10	0.10	0.10
Dispersing Agent	0.72	0.60	0.50
Defoamer	0.40	0.40	0.50
Mono Etilen Glikol (MEG)	1.00	1.50	1.50
Coalescent Agent (Texanol)	0.50	1.00	1.50
Polyurethane Thickener	0.00	0.30	0.40
Biocide	0.20	0.20	0.20
Water	25.30	23.00	15.00
Total	100.00	100.00	100.00

2.3 Dispersion Additives in Water Borne Paint Formulations

For inorganic pigments in water based paints used are the most common type polyelectrolyte dispersing additive. They are divided into inorganic and organic polyelectrolytes. Inorganic polyelectrolytes are polymeric phosphates.

Polyphosphates can be degraded hydrolysis in 8-9 pH environments or creating strong complex with transition metals in environment. It decays can lead to unexpected changes in paint rheology.

Organic polyelectrolyte dispersing additives are relatively low molecular weight polymers. Polyacrylates and copolymers of styrene-maleic are examples of organic polyelectrolytes. For example, 12 to 18 monomer units consisting of PAA dispersant usually gives the best performance. The optimum chain length of the particle surface reflects the balance between the appropriate anchoring. Low molecular weight polymers compared to high molecular weight polymer the surface adsorption is faster. In addition, in evaluating the effectiveness of dispersion of the binder are used in paint formulations wetting and dispersing properties that should be considered in. Especially the type of alkyd resin binders has good wetting properties and dispersion forces contribute significantly to the total paint formulation achieved [3].

The molecular weight of the polymeric pigment dispersant that has van der Waals attractive forces between the particles to overcome the appropriate length should be sufficient to ensure the polymer chains. If the chain is too short, polymeric dispersants can not create a sufficiently thick barrier for preventing pigment agglomeration. Therefore, very low molecular weight polymeric dispersant causes the dispersion to become unstable. If chain length is a very long, the potential of bridging increase between particles. Also the tendency to fold back on themselves causes flocculation. Therefore a high molecular weight polymeric dispersant will reduce the performance of the dispersion. Polymers with molecular weights above 106 g/mol are generally used as a flocculant, the preferred polymeric dispersant molecular weight is lower than 20,000 g/mol. For example, polyacrylic acids having lower than 15,000 g/mol molecular weight is often used in dispersion of TiO_2. Used in pigment dispersions consisting of maleic acid or methacrylic acid-acrylic acid copolymers of molecular weight 2,000 to 10,000 g/mol [11].

A long chain polymer adsorption on the surface of the many polymer segments is usually affinity with the particle. Some segments of the polymer chains to the surface even though weak affinity as a whole still has a very strong affinity with the surface. For example, the attached number of groups is 12 and the probability of each group is 20% in the case, the possibility of holding the polymeric dispersant molecules to the surface of the pigment is over 90% [11;12]. A polymeric pigment dispersant to be

adsorbed to the surface, attached group must be capable of strong adsorption to the particles. Amines, ammonium and quaternized ammonium groups, carboxylic, sulfonic and phosphoric acid groups and their salts, sulfuric acid ester groups, and phosphate functional groups which may attach to the mineral oxide particles are examples [12].

Polymeric dispersant depending on the ionic charge characteristics of the functional groups and nonionic types are available. Solution of ionic impurities and impurities on the surface or the addition of different pigments with different surface charge properties of the ionic dispersants can easily degrade the performance of the dispersion. Nonionic dispersants generally is not sensitive to pH and ionic strength changes. Ionic and non-ionic functional polymeric dispersant are taken together in order to provide better performance of pigment in dispersion [12].

2.3.1 Water borne paints performance tests

In order to determine the properties of water-based paints are tested for several performance test as listed below. These tests especially determine the dispersion efficiency and stability of the water borne paint formulations.

- Viscosity measurement
- Grindometer measurement
- pH measurement
- Hiding power test
- Gloss test
- Storage stability test (52°C, 1 month)

2.3.1.1 Viscosity measurement

Dispersions of solids in liquids, such as titanium dioxide particles dispersed in a waterborne paint formulation, are important in the manufacture and performance of paints. The viscosity of paints mainly determines the performance of the paint during the all using process, from storage to end use application. Especially, viscosity regulates the performance of coatings when especially leveling, sagging and pigment settlings are regarded. The stable water borne paint dispersions can improve process ability, storage stability and can ensure higher solids at application viscosity. The rheology of the pigment dispersion is especially practical for characterization of

dispersions due to stability and quality of dispersions can be easily measured. There are two sides of rheology of the pigment dispersion. These are the dependence of viscosity on the concentration of the dispersed phase and on shear stress and shear rate. The developing paint technology with many tools has been developed to measure viscosity such as Brookfield viscometers display in Krebs Units (KU), Centipoise (cP) and Grams (gm) units [13;14].

2.3.1.2 Grindometer measurement

The degree of pigment dispersion was expressed by a standard fineness ofgrind, i.e. the presence of oversize particles in the paint. In order to determine fineness of dispersion and detection of oversize particles in paint dispersion, grind gages called grindometer are generally used in paint industry. The gage is a steel block which is cut a wedge-shape channel, narrowing usually from the deep end to zero at the other end, while other depths and variations of dimensions of wedge-shape channel are accessible and some gages have twin channels. The gauge is shown in Figure 2.4 : and specified in ASTM Test Methodfor Fineness of Dispersion of Pigment-Vehicle Systems (D1210) is almost identical to the Hegman gauge [15].

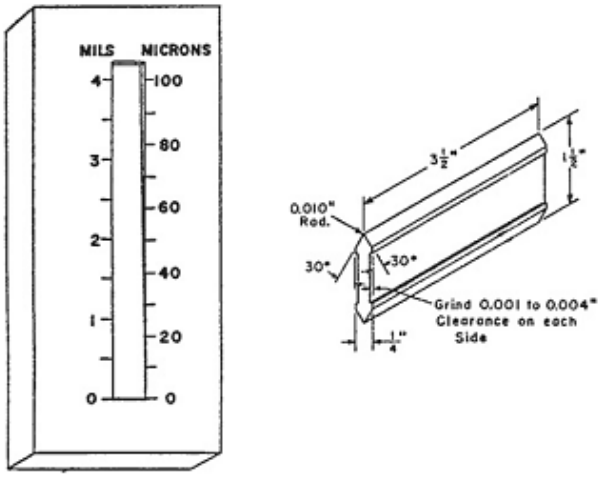


Figure 2.4 : ASTM grindometer and scraper [15].

An excess of the sample is placed in the top of the channel, it is drawn to the shallow end with a scraper. Poor milled coarse particles and agglomerates become visible at some point along the channel. The typical pattern produced by grindometer is illustrated in below figure and the fineness of particles in dispersion was 40 microns. The speed of drawdowns and the angle at which the scraper is held have no

important effect on the results. However, the time lapse between the drawdown and reading are important for reproducible results [16].

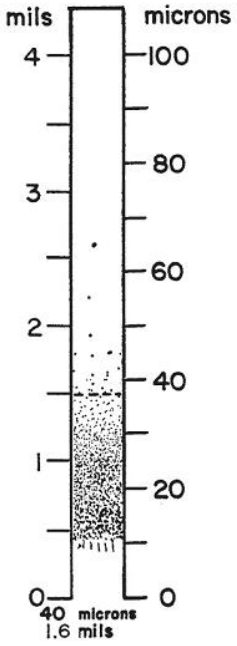


Figure 2.5 : Typical pattern produced by a dispersion gauge [16].

2.3.1.3 Hiding power test

Some of light is absorbed or reflected by the paint film before reaching the substrate when it enters a paint film. Light reflection from the paint film is understood as visibility or lack and so, mentioned as hiding. Opacity is defined as the property of a paint film which intercepts the passage of light and because of hiding the applied substrate. So that, opacity is a film property, however hiding poweris a property of the entire paint. In order to refer to both of opacity and hiding power of paint film, the generally used term is hiding [17].

The efficiency of milling and dispersion of pigments has important effect on opacity of the paint film. When the floccules of pigments due to weak forces of cohesion, the decreasing the scattering efficiency of the pigments is occurred. Accordingly, the hiding power of paint film reduces when pigments and extenders are not well dispersed [17].

The opacity is denoted photometrically as the ratio of the luminous Y-reflectance the darker over the lighter area of the test substrate, which is called contrast ratio and

referred to as the CR. CR is given in Equation 2.2. The minor CR values refer intermediate levels of contrast or weak hiding power.

$$\%\,\mathrm{CR} = \frac{\text{Y reflectance of the black area}}{\text{Y reflectance of the white area}} \times 100 \qquad \textbf{(2.2)}$$

The Y reflectance is measured with a spectrophotometer. The CR value is greater than 0.98, it is effective with colors. Furthermore, when the color difference (ΔE) is less than 1.5, it is desired for various colored paints [17].

2.3.1.4 Gloss test

The appearance of painted surface can be specified by its color and gloss characteristics. The gloss of the dried paint films is measured by a gloss meter which it is developing portable devices for varying paint applications. Single measurement angle like 60° could not ensure instrument readings of gloss that correlate well with visual observations for comparing different gloss levels. For this reason, ASTM D523 standard presents for measurement at three different angles of arrival 20°, 60° and 85° [18].

The standard claims that the 60° gloss is used for comparing most specimens and for determining when the 20° or 85° gloss may be more compatible. The 20° gloss is advantageous for comparing specimens having 60° gloss values higher than 70. The 85° gloss is most frequently performed when specimens have 60° gloss values lower than 10 [18].

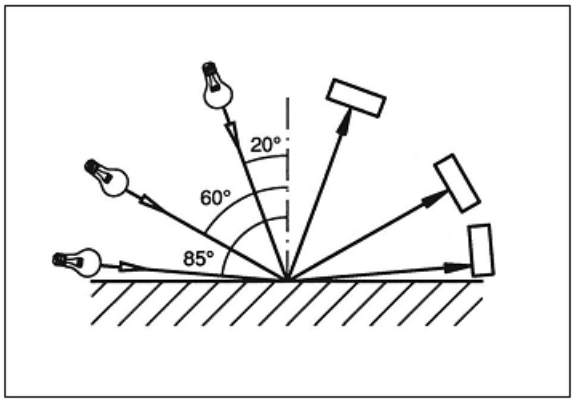


Figure 2.6 : Three measurement angles of ASTM D523.

S. Farrokhpay et al. stated that the paint gloss increases with increasing efficiency of particle dispersion in paint manufacturing. Gloss associated with the decrease in pigment aggregate number at the paint formulation. They were concluded that the variation and amount of polymeric dispersant influenced the pigment dispersion in dry paint coatings. In addition, the paint surface was roughly and its gloss value was low, when the dispersant were not used in paint formulation. In the existence of polyacrylic acid dispersant, dried paint film was smoother and so the gloss values at 60° light incident is higher than absence of polyacrylic acid dispersant [19].

2.3.1.5 Storage stability test

Storage stability test of the water borne paints covers the change in consistency andcertain other properties that may take place when the paint is stored at a temperature above 0°C. According to ASTM D1849−95 (2008), Standard Test Method for Package Stability of Paint, the storing the water borne paint for 1 month at 52±1°C simulates some of the effects of storage for 6 months to 1 year at 23±2°C. Any evidence of pressure or vacuum in the unopened containerskinning, corrosion, souring and odor of putrefaction were investigated in the stored paint samples [20].

2.4 Adsorption of Polyacrylic Acid Sodium on Mineral Surfaces

The most commonly used dispersants in paint systems with molecular weights of 1000 and 20000 g/mol ranging polyacrylic or polymethacrylic acid derivatives. These polymers are provided with water solubility by ammonium, sodium or potassium hydroxide neutralization. Sodium and potassium polyacrylatescan not be used in coating applications which is requested to very high water resistance. Sodium or potassium ions remain in the dried paint film, so it creates water sensitivity. Ammonium salt of polyacrylic acid is preferred to requiring better water resistance applications [5].

Sodium and ammonium salts of polyacrylic acid to be adsorbed to minerals in the general physical and chemical adsorption can be divided into two categories. Physical adsorption is generally a weak interaction and includes small energy changes. Chemical adsorption takes place between dispersing agent and surface by covalent attachment and it means strong interaction. Hydrogen bonding and hydrophobic interactions are the other different forces interactions. The advantages

of an adsorption mechanism other adsorption mechanisms depends on the specific conditions of polymeric dispersant agent and pigment surface. In addition many type of this interaction may be present in a system. The adsorption mechanism of sodium and ammonium salts of polyacrylic acid is by electrostatic interactions, and hydrogen bonding is by chemical interaction [11].

Electrostatic interaction is valid for ionic molecules. Attractive electrostatic forces attract ions loaded with opposite charge of the surface and accumulate on the surface. Repulsive electrostatic forces are between mineral surfaces to negatively charged anionic molecules such as polyacrylic acid.

Chemical interactions can occur between the mineral surfaces to polymeric dispersions. Cationic groups on the mineral surfaces react with polymer groups and can be formed insoluble compounds. The chemical interactions of carboxylic groups between titanium pigments and the surfaces of alumina can be mentioned. However, the chemical interaction between the carboxylic groups and the mineral surfaces is dependent on environmental conditions such as pH, ionic potency, mineral surface and carboxylate groups decomposition level of mineral surfaces.

Giving the hydroxyl groups on the surface of suspended particles or accepting a proton is called hydrogen bonding. Hydrogen bonding, acid-base interaction is part of the widely used and all of the mineral surface with polymeric dispersing agents has the ability to hydrogen bond. In the case of a negatively charged anionic polymer adsorbed on a surface, attractive forces such as hydrogen bonding can overcome electrostatic repulsion. Organic compounds, which are attached one hydrogen atom to a strong electronegative atom such as oxygen, sulfur or nitrogen atoms, and mineral surface hydroxyl (-OH) groups can form hydrogen bonding. In the polymer carboxylate (-COOH) groups can act as a proton donor or acceptor depending on the decomposition of carboxylate groups and adsorbed by hydrogen bonding with mineral surfaces of the hydro (-OH) groups [11].

The adsorption free acid groups of polyacrylic acid on kaolin particles is seen to be in Figure 2.7 :.

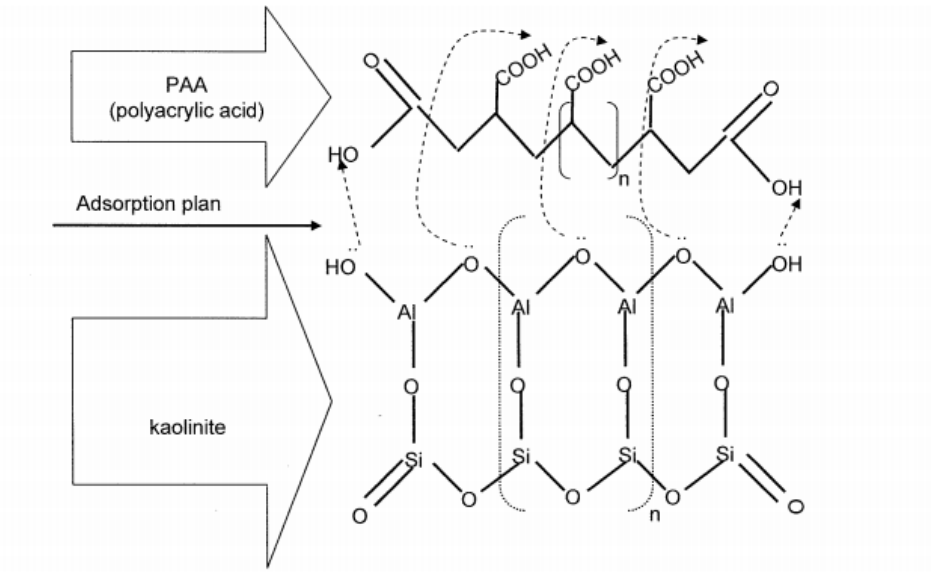


Figure 2.7 : The adsorption free acid groups of PAA on kaolin particles [21].

2.4.1 The factors of affecting adsorption

There are some parameters that guide mechanisms of NaPAA adsorption to the minerals oxide surface. These parameters can be summarized as mineral type and number of groups on the surface, chemical structure of polymer, anionic, cationic or neutral state of polymer, molecular weight of polymer, in the medium of the solvent type, medium pH and ambient temperature. It is added to the medium mineral surface properties which can be replaced with any electrolyte or surfactant. This adsorption of the polymer will be directly affected. Polymer adsorption takes place intensively on minerals which have higher zero load point (IEP). A bulk polymer of any (non-ionic) state through hydrogen bonding interactions while the anionic or cationic polymers can be adsorbed electrostatically [12].

2.4.2 The effect of pH

How change the adsorption mechanism of PAA on the oxide minerals surface depending on the pH s plotted follows as a general representation. Agglomeration of the polymer is observed the mineral surfaces at acidic pH. Reason for this, the degree of ionization of PAA is too low at acidic pH. As the pH increases the functional groups in the polymer begins to separation and to repel each other. Linear polyelectrolyte loaded in high pH on the particle surfaces of the mineral is known to also become longer. The adsorption type of the polymer is transformed joint and coil structure to long tail structure as the pH increases. Since the distance between

polymer chains with surface increases, the adsorption of polymer chains is reduced. However, due to long tail structure steric repulsion force and adsorption layer thickness increases [22].

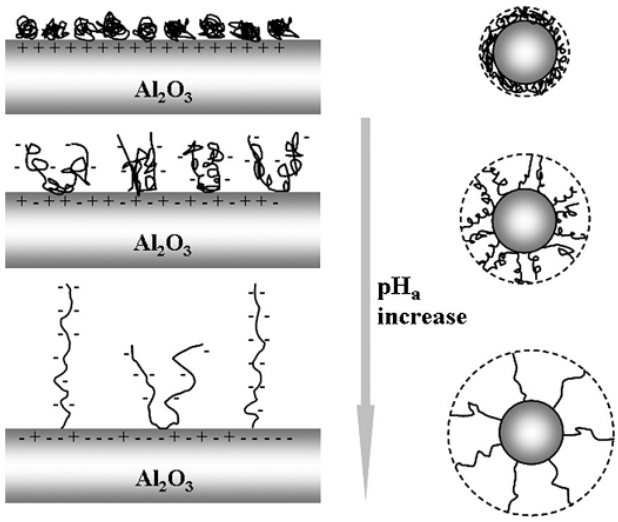


Figure 2.8 : Variation in the polymer chain structure of changing pH [22].

PH of the medium should be at a pH as high as 9 for ionization of all functional groups on NaPAA. Reason for this a carboxyl functional group on the surface of the polymer is ionized make it difficult to the side of another group ionization. These groups as $–O^-$ in the high pH, is present as OH_2^+ at low pH the retention of oxygen with a hydrogen atom [23].

Liufu et al. indicated that PAA is connecting with hydrogen bonding, electrostatic and chemical interactions to the surface of TiO_2. The adsorption density increases with increasing molecular weight of PAA and it increases the pH decreased. The thickness of adsorption layer was determined as a result of the viscosity measurements with presence and absence of PAA. The thickness of adsorption layer increases with increasing molecular weight of polymer, concentration and pH [24].

F. Karakas and M.S. Celik reported that more efficient stabilization of TiO_2 suspensions were achieved at high pH values with electro-steric repulsion. Also they were stated that NaPAA was available in long tail structure at above pH 8.5. The adsorbed NaPAA onto particle surface via hydrogen bonding and chemical interactions has effective steric forces at these pH ranges. As shown the below figure, pH of the water borne paint formulation should be above 8.5 in order to obtain

suitable for stabilization of particles. Even if, using a smaller amount of NaPAA, stabilization can be achieved at this pH ranges [25].

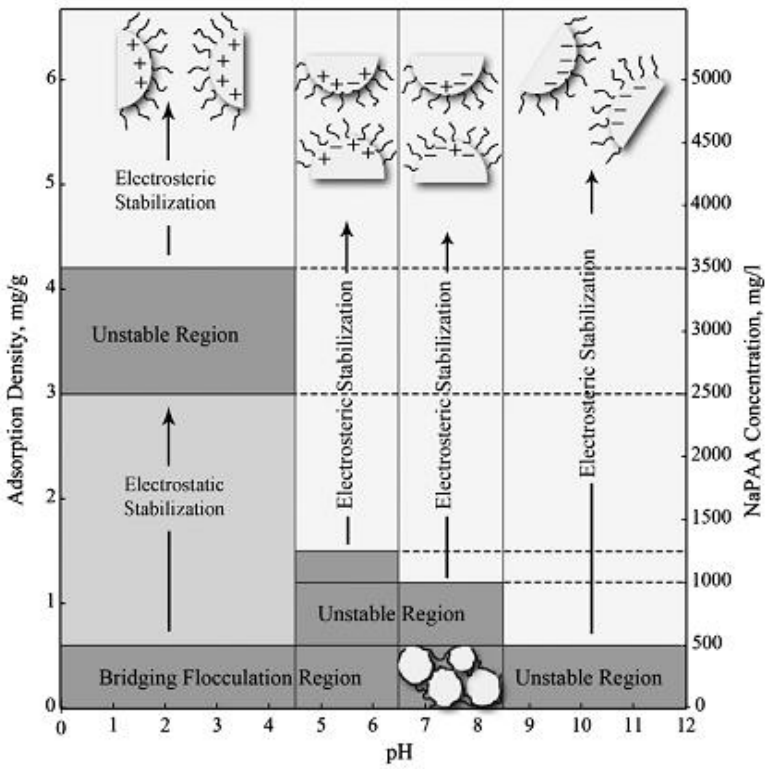


Figure 2.9 : Stabilization of TiO_2 with varying pH and amount of NaPAA [25].

2.4.3 Effect of polymer molecular weight

The molecular weight and molecular weight distribution of sodium polyacrylate polymers affect the adsorption process [26]. 4000, 2000 and 7000 g/mol in molecular weight of the different NaPAA experiments were performed by Foissy et al. It is found that the molecular weight increases, the intensity of adsorption increases [27]. However, Boisvert et al. found that the difference molecular weight absence of any effect for adsorption of NaPAA on alumina-coated TiO_2 in their study with 2100-5100 and 20000 g/mol molecular weight polymers at pH 9 [28].

Lamarche et al. reported that best efficiency in rheological properties of sodium polyacrylate polymers with the molecular weight between 2000 and 20000 g/mol was found at 2000–4000 g/mol. Polymeric dispersant chains with a molecular weight between 2000 and 4000 g/mol were also realized to fasten on the calcium carbonate energetically in a more effective way. The dispersion efficiency of sodium polyacrylate dispersants with a molecular weight between 2000

and 4000 is electrostatic repulsion between likewise charged particles. They suggested that when polydisperse polymer chains are used as a dispersant, only chains with a molecular weight of 5000 g/mol adsorb on the surface in a flat conformation while other chains stay in solution [29].

Geffroy et al. had a research on the molecular weight of sodium polyacrylate polymers affect the adsorption process on calcite surface. The adsorption of sodium polyacrylate polymers onto calcite surface first involves the adsorption of the shortest polymer chains, as these can diffuse first to the surface. They reported that when sodium polyacrylate polymers with a molecular weight below 1500 g/mol are used, the adsorption of polymers did not occur on the calcite surface. Those polymer chains were not able to disjoint CO_3^{2-} and HCO^{3-} ions and to attach onto Ca^{+} sites at the calcite surfaces. It is also express that larger macromolecules are able to replace small macromolecules attach on the surface. They found that sodium polyacrylate polymers with a medium molecular weights adsorb energetically in a more effective method on the calcite surface than larger sodium polyacrylate polymers [30].

Three different types in different molecular weight PAA used another study which was tried separately in low and high solids concentration of PAA adsorption on the TiO_2. 2000, 1000 and 11000 g/mol molecular weight Polyacrylic acid was used in the study and each adsorption isotherms for PAA were formed. Also, performed zeta potential and viscosity measurements indicated that PAA increased zeta potential in the negative direction, scrolled left iep point and significantly reduced viscosity. As a result of stabilization studies, the destabilizing effect reverse of the desired effect and causing flocculation is seen at low concentrations of PAA. In addition when low concentrations of PAA is used, it flocculates particulates by mechanism of bridge flocculation. It has provided dispersing effect and a good stabilization above a certain concentration [31].

2.5 Stabilization of Mineral Dispersions

Mineral dispersed with polymeric dispersant systems have three mechanisms electrostatic stabilization, steric stabilization and electro-steric stabilization. The following figure shows stabilization mechanism of the particle dispersion.

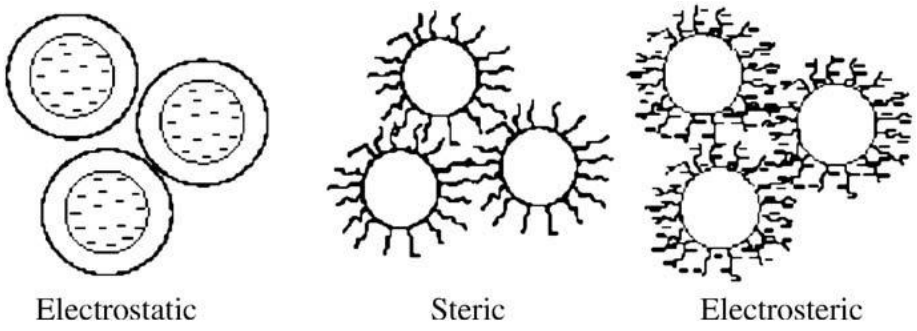


Figure 2.10 : The stabilization mechanism of the particle dispersion [11].

Ionic polymers, adsorbed onto mineral surfaces in an aqueous system at electrostatic stabilization, can be form a charged film around the particles and prevent aggregation (clumping). However, the efficiency of the stabilizing load may decrease due to external factors. This reduction may be achieved by the presence of impurities on mineral surface or in ionic solutions, or the addition different surface loading properties of different minerals or pigments to the medium.

The steric stabilization is generally thought to occur by two factors. These factors are the volume restriction of mineral surface and increasing polymer concentration which is the result of compression adsorbed layers. The activity of stabilization is enhanced by increasing adsorbed layer thickness and the particle size the increase. A dispersion comprising mineral pigment or filler have diameters of 200-1000 nm to provide sufficient stabilization of the adsorbed layer thickness must be between 10-20 nm. When titanium oxide particles are dispersed with polymeric dispersants, the larger diameter is reached. Therefore, short chain carboxylic acids are preferred in particularly the stabilization of dispersions containing nanoscale particles titanium. In the same polymer molecule is possible to provide both electrostatic and steric stabilization. While nonionic polymer dispersants are providing stabilization of the pigment particles with steric force, ionic polymer dispersant provide both electrostatic as well as steric stabilization of the pigment. In this case provided to the type of stabilization is called electro-steric stabilization [3; 11].

Combinations of steric and electrical stabilization called as electro-steric stabilization are typically considered in water borne paint systems. The zeta potential is important parameter of the stabilization of pigment dispersion in paint formulations. It could be increased with consequential adverse effect on the stabilization of pigment dispersion. On the other hand, when freely movable long molecule chains joined, the

entropy of the system was lower. In addition, the zeta potential of system was reduced and stabilization of water borne paint system was increased due to the electro-steric stabilization. The reduction of the zeta potential with the electro-steric stabilization is shown in Figure 2.11 : [32].

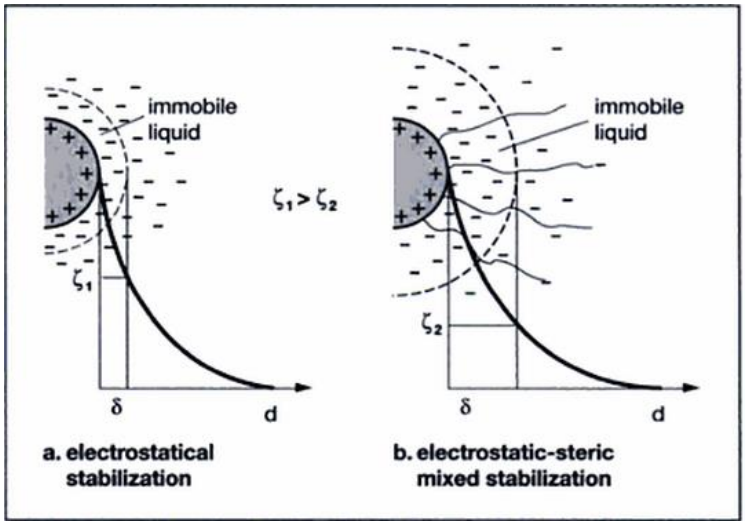


Figure 2.11 : Electrosteric stabilization effect on the zeta potential [32].

Deng et al. had a research on the stability of 40 percent by weight of $CaCO_3$ suspensions on addition of sodium polyacrylic acid has been examined using rheological measurements. In the lack of sodium polyacrylic acid, the suspension is flocculated even though the positively charge particles have a sufficient +25mV zeta potential to ensure electrostatic stabilization. When 0.1 percent by weight of NaPAA was added, suspension considerably flocculated. The zeta potential of $CaCO_3$ suspension reached much higher negative value −45mV which is more than sufficient in order to obtain electrostatic stabilization. In addition they stated that low molecular weight NaPAA chains attach to the surface of $CaCO_3$. Also the yield value of suspension versus square of zeta potential plotted in this study and they claimed that it given a non-linear curve which it explained the stability of $CaCO_3$ suspensions in the presence of NaPAA dispersant. However, they concluded that absorbed loops and tails of NaPAA dispersant molecules on surface of $CaCO_3$ were very important for stability of suspensions [33].

Qianping et al. had a study on the stabilization TiO_2 particles in TiO_2 suspensions with varying 0–1.2 % NPAA based on the TiO_2 weight. The polyacrylic acid was synthesized in isopropanol medium by using ammonium persulfate as initiator. NaPAA were as dispersant to prepare aqueous TiO_2 suspensions. The zeta potential

of TiO_2 suspensions added varying amount of NaPAA as a dispersant was measured. They reported that the absolute value of the zeta potential of the suspension and electrostatic repellent force between the TiO_2 particles were increasing with increasing amount of NaPAA. This situation inferred to obtain enhancement of the TiO_2 suspensions [34].

2.6 The Production of Polyacrylic Acid Sodium Salt Used As Dispersing Agent

Physical properties of acrylic acid given in the following table and polymerization of acrylic acid are potentially explosive exothermic reaction. The concentrated solution of the high heat of polymerization is difficult to control the polymerization reaction and uncontrollable polymerization forming cross-linked polymer can be readily gelled. When you bulk polymerization to be made, it can be performed in very small amounts under the appropriate protective measures [35].

Table 2.2 : The physical properties of acrylic acid.

MolecularWeight (g/mol)	72.06
Melting Point (°C)	13.5
Boiling Point (°C)	141
VapourPressure (kPa, 25°C de)	0.57
Heat of Polymerization (kj/mol)	76.99
Refractive Index (n_D)	1.045
WaterSolubility	Soluble

The mechanism of the polymerization of acrylic acid is rapidly progressive environment pH and significant changes in temperature and is responsive to selections solvent or solvent system. The polymerization rate at low pH is higher the speed decreases rapidly to a minimum at pH 6-7 and at pH 10 reaches the maximum speed. Sodium and ammonium salts of polyacrylic acid are produced by neutralization the polyacrylic acid with polymer caustic or ammonia. The following figure shows the sodium salts of polyacrylic acid [22].

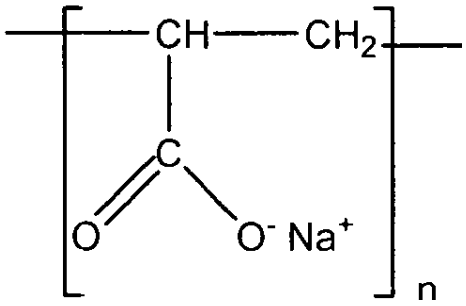


Figure 2.12 : The sodium salts of polyacrylic acid.

FTIR spectra of polyacrylic acid and the sodium salt polyacrylic acid are observed in the figure below. Since except C=C band all other bands are the same in both acrylic and polyacrylic acid. The strong two peaks of C=C band at 1617-1634 cm-1 distinguishes between acrylic and polyacrylic acid. Stretching group of C = O at 1701-1721 cm-1, asymmetrical stretching group of COO- at 1545-1631 cm-1, symmetric stretch group of COO- at about 1405 cm -1, asymmetric stretch group of CH_2 at 1458 cm-1, asymmetric stretch group of C-C-C 1152 cm-1 are shown in the following spectra [22; 36].

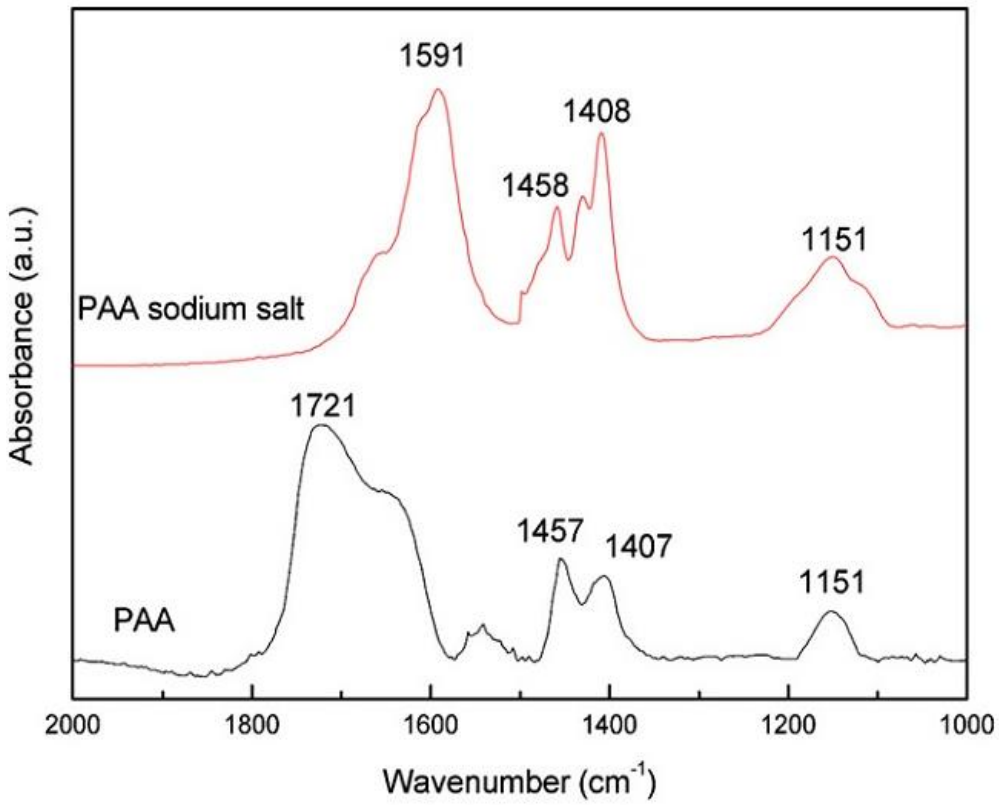


Figure 2.13 : FTIR spectra of PAA and NaPAA [22].

There are many commercially methods of acrylic acid polymerization. Water is used as solvent or to form the polymerization medium when considering the economical and environmental drawbacks for industrial scale production. However, selection of the production method is determined by the requirements of the produced polymer [37].

Polyacrylic acid is most widely used manufacturing method is free radical polymerization. Polymer can be obtained from several thousand up to several hundred thousand molecular weights. Molecular weight of PAA dispersant which is used the most common in paint formulations is 1000 and 20000 g/mol. The molecular weight can be controlled by adjusting the amount of initiator and using chain transfer agent. Polyacrylic acid dispersant used in paint formulations as well as the molecular weight distribution of the polymer chain affects the quality of the dispersion. The distribution of polymer chains is called "polydispersity index" (PDI) and is calculated by dividing the weight-average molecular weight and number average molecular weight [37].

Controlled radical polymerization has three main types nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT).

The following figure try to compare three main types of controlled radical polymerization NMP, ATRP and RAFT in the areas associated to the synthesis of high molecular weight polymers (HMW), low molecular weight polymers (LMW), end functional polymers (End Funct), block copolymers (Blocks), range of polymerizable monomers (Mon Range), synthesis of various hybrid materials (Hybrids), environmental issues (Env) and polymerization in aqueous media (Water). Three techniques have advanced largely a result of a more thorough mechanistic understanding of the pertinent phenomena in all areas. Low molecular weights and low narrow distribution chain polymers were difficult to prepare with RAFT due to strong retardation reactions. However, the suitable selection of RAFT reagents has mostly got through this problem. The cost of the end group now remains the main issue in the synthesis of low molecular weight polymers for all controlled radical polymerization methods [38].

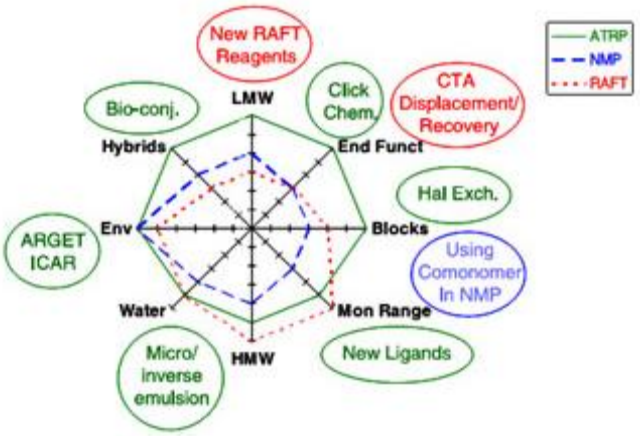


Figure 2.14 : Comprasion of RAFT, NMP and ATRP [38].

In the NMP polymerization of acrylic acid method, there is degradation problem of nitroxide in acidic medium. In atom transfer radical polymerization of acrylic acid, metal attachment to polymer can not be controlled. Therefore, the most appropriate method is RAFT method in order to produce low molecular weight and narrow distribution chain (low PDI) of polyacrylic acid [26].

2.6.1 Production method of NaPAA with RAFT Method

Reversible addition-fragmentation chain transfer (RAFT) method is a type of controlled radical polymerization and it has been discovered in 1998 by Chiefari et. al. They stated that RAFT method produces polymers with controlled molecular weight and narrow polydispersity values [38].

Due to the ability to predict the molecular weight of complex block, graft, and star polymers, RAFT method made intensive research on a polymerization process have become. In addition, the monomer and initiator specific chain transfer agent used in the reaction medium. Chain transfer agents and chain regulators are generally used thio-carbonyl-thio compounds, mercapto alcohols and acids, salts based phosphorus can be mentioned. Thiocarbonylthio compounds as; dithio esters, dithiocarbamates, carbonates tritiyo used. Mercaptoethanol and 3-mercapto propionic acid is used in mercaptans. Phosphorus based salts have been used generally sodium hypophosphite [39].

The comparison between molecular structure of polymers obtained by the RAFT method and conventional radical polymerization process is can be seen the following figure. When the chain transfer agent is used, chain length control is more effective and polymers with narrower PDI can be obtained.

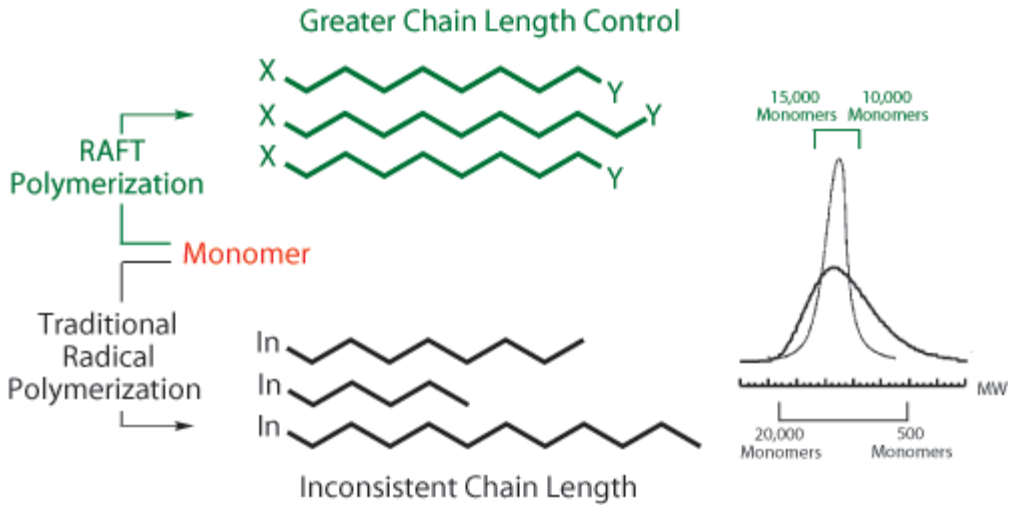
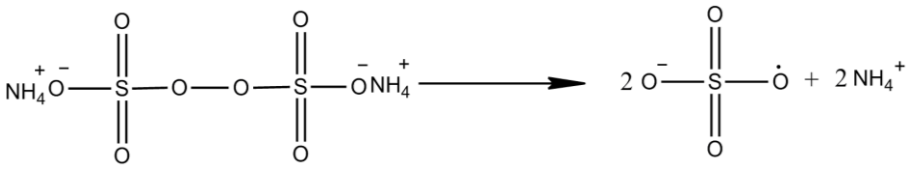


Figure 2.15 : The comparison the RAFT method and conventional method [39].

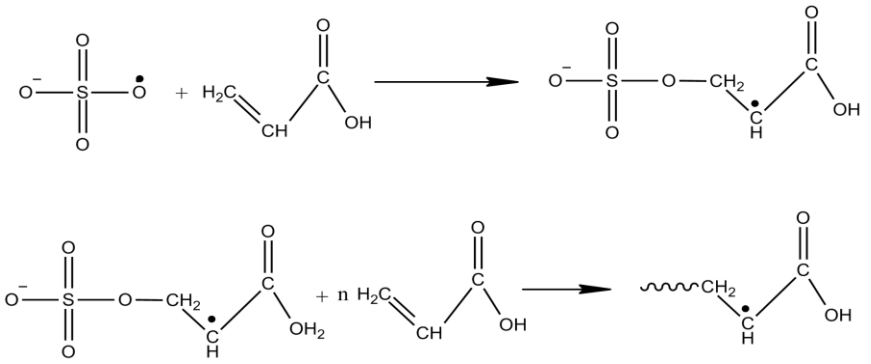
In generally, heat-activated initiators and redox initiators are used in the free radical polymerization of Polyacrylic acid. Heat-activated initiators persulphates, perphosphates, azo compounds, hydroperoxides are examples and this type of initiators are used in 50-100 °C temperature. Redox initiators are generally used to perform the polymerization at low temperatures [37].

In the RAFT polymerization of acrylic acid, a specific chain transfer agent, monomer and polymerization initiator are introduced into reaction. The initiator, APS, generates free radicals with acrylic acid monomer in initiation step as shown Equation (2.3).



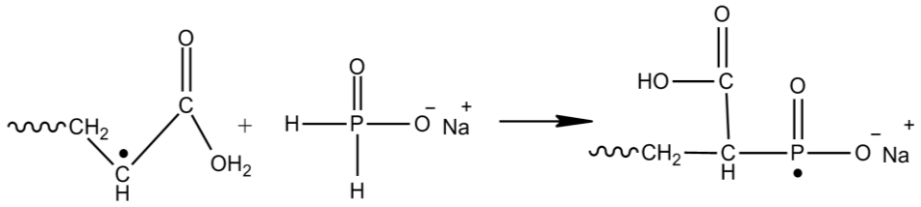
(2.3)

These free radical reacts with a monomer to produce reactive center then adding ensuingly structure to form a propagating polymer chain. In Equation (2.4), these radicals react with acrylic acid monomers and produce a propagating acrylic acid polymer chain.



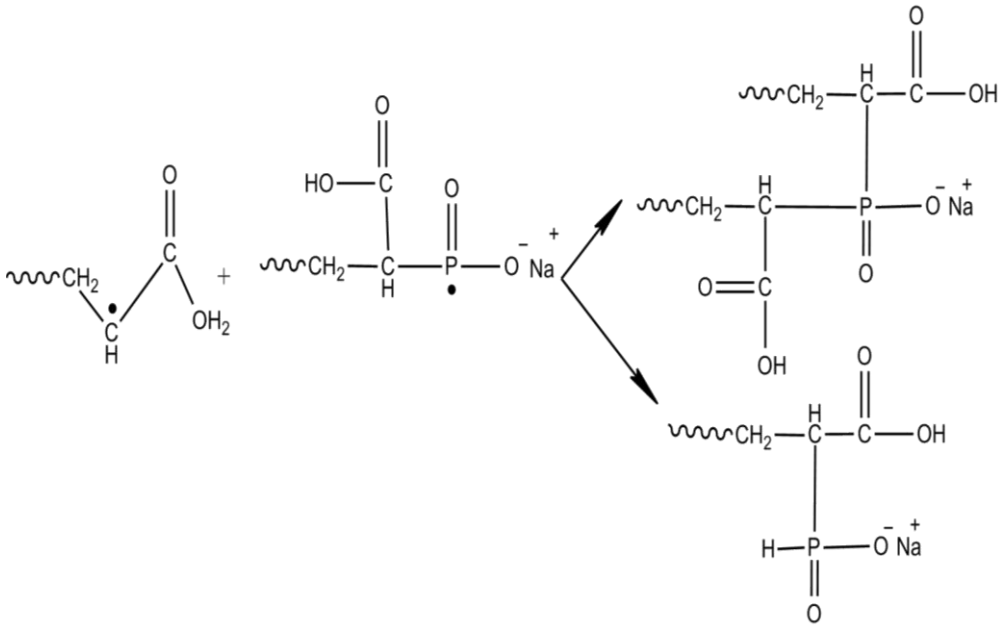
(2.4)

The propagating polymer chain attaches to the chain transfer agent or chain regulator to produce new radical group as illustrated in Equation (2.5). These new radical groups as a macro transfer agent. Then transfer reaction is accelerated and all chains make transferring chain with another at the same speed.



(2.5)

Therefore when the polymerization is terminated,all chains will have approximately the same length. Thus, lower PDI polymers can be obtained. The termination step was shown in Equation (2.6). In addition acrylic polymer chains can be terminated dialkyl phosphinate and mono alkyl phosphinate ending groups.



(2.6)

In US 5077361 patent, it was stated that phosphinate and phosphonate functionality groups in the acrylic polymer can provide desirable dispersing properties and the percent of dialkyl phosphinate groups in acrylic polymer was about 70-90% [40].

In RAFT method, many solvent or solvent mixtures may be used. Preferably water and water-alcohol mixtures are used. Methanol, ethanol, n-propanol, isopropanol and butanol are used as alcohol. Examples of other solvents are acetone, acetonitrile, benzene, hexane, toluene, formic acid, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide ethyl acetate. Molecular weight and PDI of the polymers synthesized by RAFT method depend on monomer, initiator and chain transfer agent type and concentration, the feed rate of monomer, initiator and chain transfer agent, solvent system, temperature, pressure and the time of polymerization [41].

In the patent numbered US7875213, the molecular weight of ranging from 3000 g/mol - 10 000 g/mol and low PDI polyacrylic acid sodium salt has been synthesized. In addition the viscosity of 75% by weight calcium carbonate-comprising mineral dispersion, which are prepared these polymers, was measured in 1, 3, 7, 14 and 28 days. In different molar ratio of monomer, initiator and chain transfer agent, ammonium persulfate and azo initiators experimented and 2,2-bis (propionic acid) tricarbonate was used as transfer agent. The polymer solution was cooled to room temperature, and then neutralized to pH about 8.3 with a 50% weight percent aqueous sodium hydroxide solution. Sodium salt of polyacrylic acid polymer which have molecular weight 8032 g/mol and PDI 1.16 give the best result in 28 days viscosity measurement [21].

In another study, having different molecular weight and PDI of sodium salts of polyacrylic acid synthesized by RAFT method were used in kaolin, calcium carbonate and titanium oxide dispersions. Two different chain transfer agentswhich are trithiocarbonic acid dibenzyl ester and trithiocarbonic acid bis (1-phenylethyl) ester are used. Ethanol, isopropyl alcohol, methanol and dioxane were tested to be different solvents. The lowest molecular weight was reached with isopropyl alcohol solvent. Also the dispersion viscosity in comparison with a commercial product in this study, polymer which is PDI of about 1.5 has been concluded better performance by lowering the viscosity of the dispersion. In this study, the slurries of mineral solid content was 66% percent by weight of kaolin, 68% percent by weight of calcium carbonate, 75% percent by weight of titanium oxide in water. The varying amount of

PAA is added as a dispersant. Brookfield viscosities were measured at 10 and 100 rpms and it showed a characteristic bell curve. They indicated that viscosities were high due to the presence of partially flocculated particles when added amount of PAA was too low. Then, the viscosity decreases with a certain amount of PAA until a minimum is achieved. After, the viscosity increases due to the presence of non-adsorbed polymer in mineral solution. They compared the dispersion performance of polymer synthesized via RAFT method to polymer prepared by a conventional living radical method and stated that the desired amount, where minimum viscosity is reached, is lowered as a result of the narrower molecular weight distribution in RAFT method. Most polymer chains have the right molecular weight to promote to the adsorption process [26].

In the study of Dongkang et al (2008), acrylic acid homo-polymer and acrylic acid-unsaturated ester copolymers were synthesized for dispersion of calcium carbonate. The viscosity of dispersions containing 80% by weight of calcium carbonate was observed relative to the amount of dispersant increasing. Optimal operating parameters are as the initiator of the monomer 4% ammonium persulfate, as chain transfer agent isopropyl alcohol/water mixture is 1.25 percent, as a neutralizer sodium hydroxide was used. In this study, sodium salt of polyacrylic acid showed significantly better dispersant property than ammonium salt of polyacrylic. In acrylic acid-unsaturated ester copolymer, copolymer which is monomer ratio 4:1 showed better dispersant property [42].

In numbered patent 2012/0199783, mercaptoethanol and sodium hypophosphite as the chain transfer agent was used. The acrylic acid polymerization is carried out at 102°C and 59% solution of sodium hypophosphite is used. Acrylic acid was fed into the system in 4 hours. 7% solution of sodium peroxodisulfate which is used as initiator was fed 3.75 hours. Sodium hypophosphite solution was fed to 3.75 hours. At the end of polymerization of 50% neutralization with sodium hydroxide was made 102°C. Synthesized polymer has a molecular weight of 2000 g/mol and PDI is 1,4 [43].

In anotherexperiment, polymerization was carried out at 99°C and used 2-mercaptoethanol as a chain transfer agent. Acrylic acid was fed into the system in 5 hours. 7% solution of sodium peroxodisulfate was fed 4.75 hours. 2-mercaptoethanol

was fed to 5.75 hours. The reaction mixture was cooled to 80 ° C then the azo initiator was added and the polymerization continued for 1 hour [43].

RAFT method offers great potential for large scale acrylic acid polymerization reactions. However, the polymeric chains produced via RAFT method contain the thiocarbonyl-thio chain transfer agent as the end group. These RAFT agents are costly, unstable long time, highly colored and strong odor due to decomposition of thio compounds to produce sulfur compounds. In some application, the presence of strong odor and color may also unwilling in the resulting polymer. In addition the chain transfer agent is not easly recovered at the end of the polymerization. Also, recovery process of this compounds may increase cost of the poymerization process [44].

2.6.2 Production method of NaP(AA-MA) with RAFT Method

The most used acrylic acid containing dispersion agent is maleic acid-acrylic acid copolymer which is 2000 to 10000 g/mol molecular weight [11]. Low molecular weight acrylic acid-maleic anhydride copolymer sodium salts are functional as scale inhibitors, detergent additives and dispersing agent. Molecular weights below 50000 g/mol are essential in order toobtain stable dispersions. Especially low molecular weights about 10000 g/mol are better dispersion efficiency [45].

Table 2.3 : The physical properties of maleic anhydride [46].

MolecularWeight (g/mol)	98.06
Melting Point (°C)	52.8
Boiling Point (°C)	202
VapourPressure (kPa, 25°C de)	0.20
Heat of Polymerization (kj/mol)	14
Refractive Index (n_D)	1.515
WaterSolubility	Hydrolyzes

The sodium salt of acrylic acid-maleic anhydride copolymer is an effective dispersant for inorganic pigments and fillers at a wide pH range. The chemical structure of acrylic acid-maleic anhydride copolymer and its sodium salt is illustrated in Figure 2.16 :.

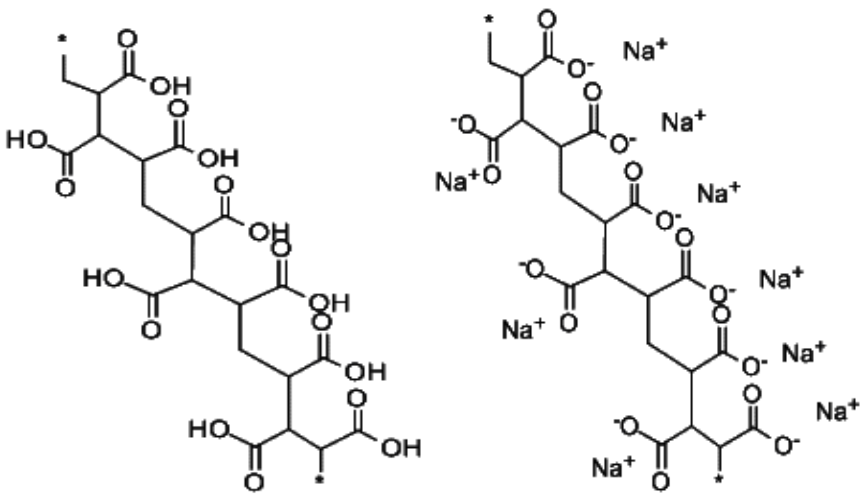


Figure 2.16 : The chemical structure of P(AA-MA) and NaP(AA-MAA) [47].

The stability of the suspension is influenced amount of anionic carboxylic group. The average molecular weight and the PDI strongly influence the suspension stability, and the viscosity decreases with the decrease in PDI [39; 48]. Viscosity and zeta potential of the suspension weredecreased remarkably withacrylic-maleic anhydride copolymer. The thixotropy of dispersion with acrylic-maleic anhydride copolymer synthesized by RAFT polymerization islitter than conventional polymerization method. Also suspensions prepared by RAFT polymerization much more stable due to the low PDI of the dispersant formedmuch more uniformity electrostatic force with particles, which reduced the aggregation of the chargedparticles, offering a reduced thixotropy loop.

In order to obtain low molecular weights copolymer, chain transfer agents are used in polymerizationin the patent numbered EP0510831. Sodium hypophosphite is commonly suitable chain transfer agent. Also, sodium hypophosphite offers phosphinate and phosphonate functionality into polymers. This phosphinate and phosphonate functionality presents better performance in some usage area especially dispersion. The used amount of sodium hypophosphite changes with demanded molecular weights of polymer. In experiment part of this patent, maleic anhydride monomer amount was 30 percent and acrylic acid monomer amount was 70 percent by weight of copolymer. Maleic anhydride monomer, deionized water and 50% solution of sodium hydroxide as a neutralizer were added polymerization reactor. The neutralizer sodium hydroxide solution was added 40 percent based on amount of maleic anhydride monomer. Acrylic acid monomer, chain transfer agent and initiator were feed separately over two hours. The 8% solution of sodium persulfate is as

initiator and was used in amount about 5.3 percent by weight of total monomer. The 48% solution of agent sodium hypophosphite amount was about 40 percent by weight of total monomer. The copolymerization reaction of maleic anhydride acrylic acid was carried out at 90° C and the total reaction time was about 150 minutes. The molecular weight of resulting copolymer was analyzed by Gel Permeation Chromatography and was about 1200 g/mol [45].

There are some disadvantages of using chain transfer agents like thiocarbonylthio compounds. One disadvantage of RAFT polymerization for producing low molecular weight acrylic acid homo polymer and copolymer is highly cost of thiocarbonylthio compound based chain transfer agents used. Moreover, this sulfur containing thiocarbonylthio compound based chain transfer agents give undesired odor to acrylic acid homo polymer and copolymer for some applications. They are deactivated in further polymerization steps. In order to remove these groups, additional costly reaction steps are required with hydrogen peroxide or amines. In the cause of obtaining inexpensive low molecular weight acrylic acid homo polymers and copolymers are used water soluble chain transfer agents as mercaptoethanol and sodium hypophosphite.

Shoufa Z.et al. synthesized NaP(AA-MA) as dispersant forraw ceramic suspension via RAFT polymerization. They examined the static viscosity, zeta potential, rheological behavior and sedimentation measurements of poly (acrylic acid-co-maleic anhydride) modified ceramic suspension. They used S,S'-Bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate as chain transfer agent. The number average molecular weight of thesynthesized P(AA-MA) was 14348 and PDI was 1.19. They claimed that the amount of used dispersant influenced the suspensions stability importantly. In order to obtain lowest static viscosity and the highest stability, the amount of dispersant was 0.3 wt.% [48].

The FTIR spectrum of P(AA-MA) was shown in the Figure 2.17 :. Stretching group of O-H at 3373 cm^{-1}, bending vibration group of C-H at 2958 $cm^{-1}$and 1406 cm^{-1}, the symmetric and asymmetric stretching vibration of C = O groups at 1649 cm^{-1} and 1552 cm^{-1} are shown in the following spectra. There was no absorption peaks at 1820 cm^{-1}~ 1840cm^{-1} of the anhydride groups and 665 cm^{-1} to 995cm^{-1} of the C = C groups of maleic anhydride monomer in the synthesized polymer [48].

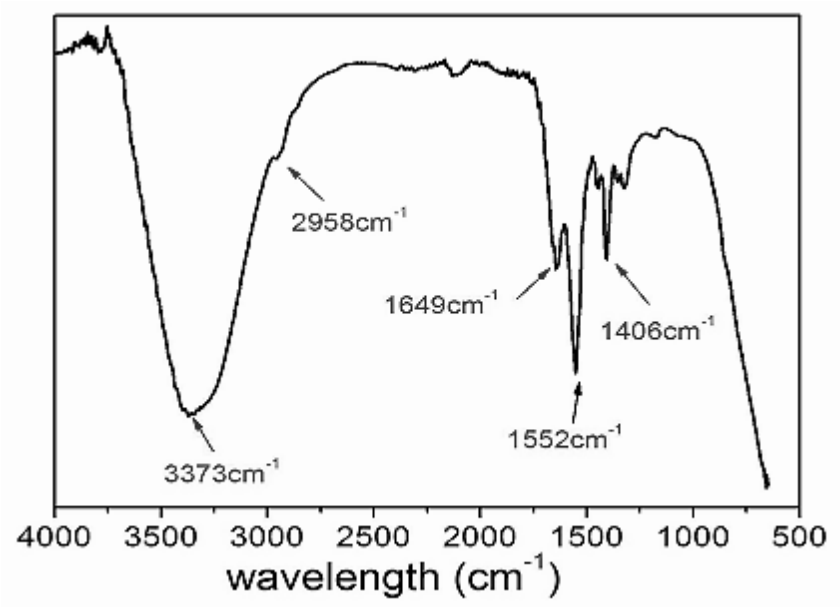


Figure 2.17 : FTIR spectra of P(AA-MAA) [48].

3. EXPERIMENTAL

3.1 Chemicals Used

3.1.1 Acrylic acid (AA)

The used acrylic acid monomer (AA) was supplied from QUIMIDROGA S.A. Its assay is minimum weight percentage of 99.5. Its molecular formula is $C_3H_4O_2$ and molar mass is 72.06 g/mol. Its melting point is 14°C and specific gravity is 1.05 g/cm^3.

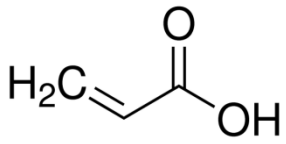


Figure 3.1 : Acrylic acid structure.

3.1.2 Ammonium persulfate (APS)

Ammonium persulfate was used as a heat activated initiator in polymerization. It was the product of Ak-Kim Kimya San. ve Tic. A.Ş. with a min. ≥% 99 solid form. Its molecular formula is $(NH_4)_2S_2O_8$ and molar mass is 228.2 g/mol.

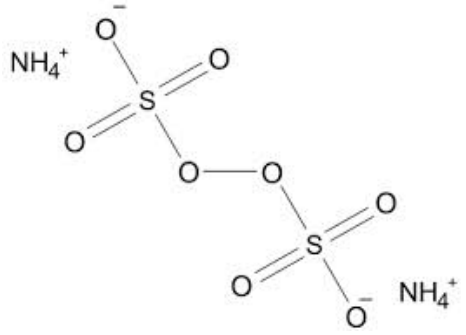


Figure 3.2 : Ammonium persulfate structure.

3.1.3 Sodium hypophosphite (NaHyp)

Sodium hypophosphite was supplied from Acar Chemicals and used as chain transfer agent. It is the sodium salt of hypophosphorous acid and often encountered as the monohydrate $NaPO_2H_2.H_2O$ that is molecular weight 105.99 g/mol. Moreover, it is a

solid at room temperature, appearing as odorless white crystals. It is soluble in water and easily absorbs moisture from the air.

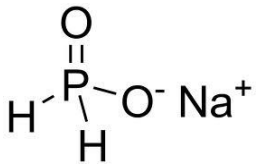


Figure 3.3 : Sodium hypophosphite structure.

3.1.4 Sodium hydroxide (NaOH)

Sodium hydroxide also known as caustic soda is an inorganic compound with the chemical formula NaOH. It was the product of Ak-Kim Kimya San. ve Tic. A.Ş. with a 32% concentration. It was used for the pH adjustment during the sythezing of NaPAA and NaP(AA-MA).

3.1.5 Isopropyl alcohol (IPA)

Isopropyl alcohol was supplied from Arkem Kimya A.Ş. and was used as solvent with aqueous medium. It is the molecular formula C_3H_7OH and is boiling point 82.6°C.

3.1.6 Maleic anhydride (MA)

Maleic anhydride is an organic compound with the formula $C_2H_2(CO)_2O$ and is the acid anhydride of maleic acid. Maleic anhydride is a white solid with a pungent odor. Its molar mass is 98.06 g/mol and melting point is 52.8°C. Its specific gravity is 1.48 g/cm^3. It was supplied from Kolsuzlar Kimya San. ve Tic. A.Ş.

Figure 3.4 : Maleic anhydride structure.

3.1.7 Hydrogen peroxide

Hydrogen peroxide is a chemical compound with the formula H_2O_2. It was the product of Ak-Kim Kimya San. ve Tic. A.Ş. with a 50% concentration. It was used for catalytic oxidation of aqueous maleic acid.

3.1.8 Chemicals used in prepearing paint formulation

In this study, 5-micron calcite, hydrous kaolin and talk were used as extenders in paint formulation and were supplied from OMYA Madencilik A.Ş. Titanium dioxide was used as a white pigment and was supplied from Dupont Türkiye Kimyasal Ürünler San. ve Tic. A.Ş. It is rutile minerals form and its refractive index 2.73. PRIMAL CM-219EF Emulsion was used as acrylic-styrene copolymer binder. CELLOSIZE QP 30000H hydroxyethyl cellulose is a medium high molecular weight cellulosic polymer with high thickening efficiency useful for general thickening of waterborne systems. Both of them were supplied from The Dow Chemical Company. All of the below chemicals were supplied from Teha Turkuaz. Sodium hexametaphosphate's trade name is Calgon used for water softener. Agitan 731 is a blend of modified organo polysiloxanes with nonionic alkoxylated compounds used as antifoam additive in paint formulations. Texanol is generally used for coalescent agent in paint formulations. It is a ester alcohol and its chemical structure (2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate). Polyurethane thickener is used to thicken and stabilize latex paints by increasing low shear viscosity. BERMODOL PUR 2102 was used as a thickener in formulations. Monoethylene glycol was used as anti-freezing in paint formulations. The used biocide's trade name is ACTICIDE and it was supplied from THOR GMbH.

3.2 Used Equipment

3.2.1 Basket heater with magnetic stirrer

Its trade mark is Heidolph MR. It was used for heating for the polymerization acrylic acid and copolymerization of acrylic acid-maleic anhydride and sodium salt of its with the condenser. Temperature was set to 80 ^{0}C during the reaction. This instrument can be heated to a maximum temperature of 300°C.

3.2.2 Mechanical mixer

Its trade mark is IKA RW16 and mixing rate is 2400 rpm. It was used for polymerization reaction and preparing of paint formulations.

3.2.3 pH meter

Its trade mark Hach Lange HQ40. The pH meter was used measuring and adjusting the pH of the PAA and P(AA-MA) obtaining sodium salts of PAA and P(AA-MA) with sodium hydroxide and measuring the pH of calcite slurries and prepared water borne paint formulations.

3.2.4 Viscometer

Brookfield Model DV-II Viscometer was used to measure the viscosity of polymer at the end of the polymerization and neutralization with NaOH. Moreover, viscometer was used to measure the viscosity of calcite slurries and prepared water borne paint formulations.

3.2.5 Zeta potential meter

The Mütek SZP-06 trade mark System Zeta Potential was used to identifies the surface charges of calcite slurries presence of varying amount of synthesized NaPAA and NaP(AA-MA).

Figure 3.5 : The Mütek SZP-06 trade mark system zeta potential meter.

3.2.6 Precision balance

The trade mark of trebuchet is Sartorius CPA 2245.

3.2.7 Solid content analyzer

Sartorius MA 35 is a rapid dryer and was used to determine the solid content of polymers.

3.2.8 Fourier Transform Infrared Spectroscopy (FTIR-ATR)

The trademark of the FTIR is Nicolet Nexus. FTIR measurements of PAA and P(AA-MA) and its sodium salts were done to validation the synthesis.

3.2.9 Gel permeation chromatography (GPC)

All molecular weights of were determined via Viskotek VE2001 GPC Max brand gel permeation chromatography. The GPC conditions used are as follows four detectors: Malvern brand right and left angle light scattering dual detectors (RALS and LALS Detectors), Viskotek VE 3580 brand refractive index detector (RI detector), Viskotek UV 2600 brand ultraviolet detector and Viscometer detector. The GPC was operated at 35° C and at a flow rate of 0.7 ml/min. The eluent used was the aqueous solution admixed with phosphate buffered saline (PBS) tablet that contains 0.01 M phosphate buffer, 0.0027 M potassium chloride and 0.137 M sodium chloride and pH 7.4. The GPC was calibrated with narrow standard, Poly(ethylene oxide) 19K, and checked calibration results with broad standard, Dextran 65K. Absolute molecular weight and molecular weight distribution of poymers were found via tetra detection of RALS and LALS, RI, UV and viscometer detectors.

3.2.10 Color measurement spectrophotometer

HunterLab ColorQuest XE is a color measurement spectrophotometer. It is used to measure opaque, transparent and translucent solids and liquids for properties such as reflected color, opacity, strength, transmitted color, APHA and haze. It was used for opacity measurements. The opacity is expressed as the ratio of the luminous Y-reflectance the darker over the lighter area of the test substrate.

Figure 3.6 : HunterLab ColorQuest XE color measurement spectrophotometer.

Before the measurements of the opacity, the paint films were applied to the Sheen brand hiding power cards via four sided film applicator. Untreated and treated hiding power cards are illustrated in Figure 3.7 :.

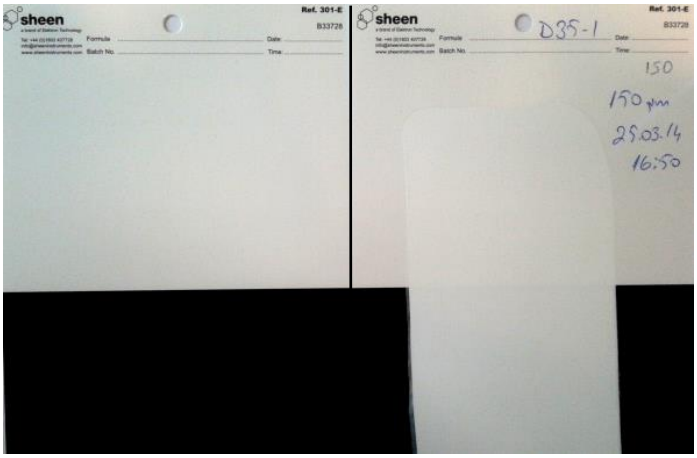


Figure 3.7 : Untreated and treated hiding power cards.

3.2.11 Grindometer

The grinding quality of fillers and pigments in paint formulation is essential for optimal dispersion. In order to determine fineness of dispersion and detection of oversize particles in paint dispersion, grindometer measurements of paint formulations were realized with Sheen brand Grindometer. The test consists of placing a small volume of paint formulation on the deep end and drawing it with a straight scraper toward the shallow end. The position on the scale where oversize particles and their tracks appear can be rated for determination of dispersion.

Figure 3.8 : Grindometer with scraper.

3.2.12 Four sided film applicator

A film applicator is used to spread paint equally over a surface. The standard procedure for testing paint film is to create a standardized test film of the substance, usually on hiding power cards. In order to provide the uniform film thickness, a film applicator is normally used to maintain a constant film thickness. Four sided film applicator has four application sides for appliying paint films with four different constant thickness. The Sheen brand four sided film applicator was used for obtaining 150 and 200 microns paint films.

Figure 3.9 : Four sided film applicator.

3.2.13 Gloss meter

Gloss measurement of paint applied glass substrates was realized with a BYK Gardner brand portable gloss meter.

Figure 3.10 : Portable gloss meter.

3.2.14 High Performance Liquid Chromatography (HPLC)

HPLC is an instrumental analysis used for separating the components in a mixture, identifying and quantifying each component. The Shimadzu brand HPLC system was used to determine conversions of polymerization of acrylic acid and copolymerization of acrylic-maleic anhydride. The conversion was determined by integration of the peak of acrylic acid in HPLC (Nucleosil 5 C18 column, UV detector and room temperature) using an isocratic water/phosphoric acid (0.1% v:v)/acetonitrile (10% v:v) mobile phase and 1 mL/min feeding.

Figure 3.11 : The Shimadzu brand HPLC system.

3.3 Synthesis of the Sodium Salt of Polyacrylic Acid

A three-necked round bottomed flask initially charged with 360 g of deionized water, varied amount of IPA as a solvent and varied amount of sodium hypophosphite as a chain transfer agent. IPA was added in two diffrent contents by weight according to the total reaction mixture (5 wt% and 10 wt%). NaPAA was synthesized in five different amount of chain regulator agent contents by weight according to the total weight of reaction mixture (0.05 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt%). The mixture was heated to 80°C. The temperature of the reaction could not extremely increase due to the boiling point of IPA at 82.6° C. Evaporating IPA was refluxed during the polymerization by condenser. At this temperature, varied amount of a 10% by weight aqueous ammonium persulfate solution as initiator and 566 g of acrylic acid monomer were added different feeding time. APS was used in four different initial feed initiator contents by according to the weight ratio of acrylic acid monomer (APS/AA %: 2.5%, 5%, 6% and 7.5%). The feeding time of monomer was varied 4.5, 5.5 and 6.5 hours. The feeding of initiator was finished about 15 minute after finishing of monomer feeding. After completion of feeding, mixture was mixed

about one hour at 80°C. When finished, the IPA with some water would be distillated from the system by using distilling apparatus under nitrogen feed. Lastly, vacuum was applied at 80°C about 10 minutes. Then the pH of the system would be adjusted to 7–8 by using NaOH (32%) solution after the system being cooled to 30°C. The finally obtained dispersant was a viscous, slightly reddish, transparency liquid.

Table 3.1 : Contents of polyacylic acid dispersant samples.

Synthesized Polyacrylic Acid Polymers		NaHyp (wt %)	APS/Acrylic acid monomer weight ratio (wt %)	Feeding Time Of Monomer	IPA (wt %)
S1	NaHyp 0	0	5	5.5	10
S2	NaHyp 0.05	0.05	5	5.5	10
S3	NaHyp 0.10	0.10	5	5.5	10
S4	NaHyp 0.15	0.15	5	5.5	10
S5	NaHyp 0.20	0.20	5	5.5	10
S6	APS/AA 2.5	0.15	2.5	5.5	10
S7	APS/AA 5	0.15	5	5.5	10
S8	APS/AA 6	0.15	6	5.5	10
S9	APS/AA 7.5	0.15	7.5	5.5	10
S10	Feeding 4.5	0.15	6	4.5	10
S8	Feeding 5.5	0.15	6	5.5	10
S11	Feeding 6.5	0.15	6	6.5	10
S12	IPA 5	0.15	6	5.5	5
S8	IPA 10	0.15	6	5.5	10

In order to determine optimal polymerization parameters, NaPAA was synthesized in four different ways which were varying amount of chain transfer agent, sodium hypophosphite, (0.05 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt%), ratio of initiator and monomer (APS/AA %: 2.5%, 5%, 6% and 7.5%), feeding time of monomer (4.5, 5.5 and 6.5 hours) and amount of solvent, IPA, (5 wt% and 10 wt%).

3.4 Synthesis of the Sodium Salt of Acrylic Acid-Maleic Anhydride Copolymer

A three-necked round bottomed flask initially charged with 200 g of deionized water, 134 g IPA, 140 g NaOH, 10.5 g H_2O_2 and varied amount of a maleic anhydride. The copolymer of acrylic acid-maleic anhydride was synthesized in two different acrylic acid-maleic anhydride monomers ratio (AA/MA: 1:1 and 1:0.5). The temperature of the reaction could not extremely increase due to the boiling point of IPA at 82.6° C. Evaporating IPA was refluxed during the polymerization by condenser. After completion of feeding, mixture was mixed about one hour at 80°C. When finished, the IPA with some water would be distillated from the system by using distilling apparatus under nitrogen feed. Lastly, vacuum was applied at 80°C about 10 minutes. Then the pH of the system would be adjusted to7–8 by using NaOH (32%) solution after the system being cooled to 30°C. The finally obtained dispersant was a viscous, slightly yellowish and transparency liquid.

In order to determine acrylic acid-maleic anhydride monomers ratio, the copolymer of acrylic acid-maleic anhydride was synthesized in AA/MA: 1:1 and 1:0.5 ratio. Additionally, the AA/MA: 0.5:1 ratio was tried but the product crystallized at room temperature due to crystallization tendency of the highly amount of maleic anhydride at room temperature.

Table 3.2 : Contents of acrylic acid-maleic anhydride copolymer dispersant samples.

Synthesized AA-MA Copolymers	AA/MA Monomer ratio	Feeding Time of AA	IPA (wt %)	APS/Monomer weight ratio (wt %)	NaHyp (wt %)
C1	1:0.5	6	10	5	0.15
C2	1:1	6	10	5	0.15

3.5 Characterizations of Samples

3.5.1 FTIR-ATR spectrophotometric analysis

The structures of the specimens were characterized by means of Fourier Transform Infrared (FTIR-ATR) spectroscopy. IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample.

The analysis of samples was carried out with this method by identification of functional groups. It is based on the excitation of IR beams of molecules (with 4000 – 600 μm wave length) to vibration and rotation levels by its adsorption. For molecular substances infrared absorption, emission and reflection spectrums are explained on the assumption that spectrums are stemmed from various changes on energy, which is enabled by moving of molecules from one vibration or rotation energy level to other. Wave numbers are obtained by Fourier mathematical modeling method. With this method, analysis has been realized by defining the functional groups of molecules.

3.5.2 High performance liquid chromatography (HPLC)

In this study, HPLC was used to determine conversions of polymerization of acrylic acid and copolymerization of acrylic-maleic anhydride. The conversion was determined by integration of the peak of acrylic acid in HPLC (Nucleosil 5 C18 column, UV detector and room temperature) using an isocratic water/phosphoric acid (0.1% v:v)/acetonitrile (10% v:v) mobile phase and 1 mL/min feeding. Each 20 mg samples of PAA and P(AA-MA) were diluted 20 g HPLC grade Acetonitrile. The mixture was slowly mixed for 24 hours in order to completely remove residual acrylic acid in polymer sample. Then, in order to prevent blocking of the column, supernatants were filtered by a PTFE membrane filter with 0.45-micron pore size. Measurement conditions are 35°C temperature, a flow rate of 1.0 mL/min and 10-microliter injection volume.

3.5.3 Gel permeation chromatography (GPC) analysis

Gel permeation chromatography (GPC) is an established method of determining the molecular weight of polymers. GPC is a fractionation technique so it determines not

only the average values but also the complete distribution of molecular weights. However, GPC only gives relative molecular masses in its conventional form such as using a single refractive index detector. In order to overcome this limitation and meet the growing demand for the characterization of increasingly complex polymers, detectors sensitive to molecular weight, such as light scattering detector and viscometer, can be used in GPC. It is advantageous to use light scattering to determine molecular weights provided the signals are sufficiently intensive strong. Triple detection combines these detection capabilities in to a single system to give molecular weight and structure without limitations. In this way, absolute molecular weight distributions can be obtained, as well as distributions of molecular weight and viscosity via tetra detection of RALS and LALS, RI, UV and viscometer detectors. Moreover, the Mark-Houwink plot can be constructed giving further structural information, such as the degree of polymer branching.

The GPC was operated at 35° C and at a flow rate of 0.7 ml/min. The eluent used was the aqueous solution admixed with phosphate buffered saline (PBS) tablet that contains 0.01 M phosphate buffer, 0.0027 M potassium chloride and 0.137 M sodium chloride and pH 7.4.

The GPC measurements of molecular weight and PDI measurement methods were carefully analyzed because of their critical to the rest of this study. Especially, for low molecular weight samples GPC of polyelectrolytes is more difficult than GPC of neutral polymers due to not separating the polymer from the supernatant by precipitation. Therefore, the GPC was calibrated with narrow standard, Poly(ethylene oxide) 19K, and checked calibration results with broad standard, Dextran 65K. Absolute molecular weight and molecular weight distribution of poymers were found via tetra detection of RALS and LALS, RI, UV and viscometer detectors.

In order to determine the molecular weight and molecular distribution of synthesized PAA,P(AA-MA), NaPAA and NaP(AA-MA), Viskotek VE2001 GPC Max was used as follows tetra detection of RALS and LALS, RI, UV and viscometer detectors.

3.5.4 Viscosity measurements of calcite slurries

The viscosity of calcite slurries was measured using a low shear viscometer Brookfield Model DV-II at 60 rpm and 20 °C in order to determine dispersion efficiency of synthesized NaPAA polymers. The mineral solid content of slurry was

66 weight of percent 5 micron $CaCO_3$ in the dispersion experiment. Then, the slurry and synthesized NaPAA and NaP(AA-MA) dispersant agents were mixed together in a dispersion bowl until the slurry became homogeneous for 20 minutes at 2000 rpm with mechanical mixer. The viscosity of calcite slurries was then recorded at 20 °C, and varied amount of NaPAA was added again for creating the curve of viscosity versus NaPAA dispersant agents concentration.

3.5.5 Zeta Potential measurements of calcite slurries

The surface charge is the overall charge of a solid particle in an aqueous solution. The majority of suspended particles and fillers carry a negative charge, while most additives are cationic. The dispersion of fillers and pigments in water borne paints shows a tendency to unstable when particles aggregate depending on the magnitude of the zeta potential of the particles. The zeta potential of calcite suspensions added varying amount of NaPAA and NaP(AA-MA) dispersant agents was measured with zeta potential meter in order to examine stabilization of calcite slurries.

3.6 The Performance Test of Waterborne Paint Formulations

Grindometer measurement, hiding power test, viscosity measurements and storage stability measurements were realized for invistigating dispersion performance of prepared water borne paint formulations which were prepared with synthesized NaPAA polymers and NaP(AA-MA) copolymers as dispersant agent.

3.6.1 The preparation of waterborne paint formulations

A sample formulation of water borne white plastic paint which has 74 PVC value is choosed in order to examine the performance of waterborne paint formulations. Waterborne paint formulations were prepared with synthesized NaPAA polymers and NaP(AA-MA) copolymers as dispersant agent. Paint formulations were prepared according to below table and the amount of the prepared formulations was 500 g.

At the first step, 100 g water, 0.5 g Calgon, 2 g HEC, 0.5 g sodium hydroxide, 3 g synthesized polymers as dispersant agent, 2 g defoamer Agitan 731 were mixed together in a dispersion bowl until the slurry became homogeneous for 10 minutes at 1000 rpm with mechanical mixer. The second step is the mill base step of the paint manufacturing. In mill base step, the mechanical energy disperse agglomerates of

pigments and fillers by this way the particle size of them are decreased. 60 g TiO_2, 192 g calcite, 15 g talk and 20 g kaolin were added the slurry as pigment and fillers of the paint formulation. Then, the slurry was mixed for 20 minutes at 2000 rpm. The last step is let-down step of the paint manufacturing. In let-down step, binder and additives participate in paint formulation. 75 g PRIMAL CM-219EF Emulsion as acrylic-styrene copolymer binder, 7.5 g MEG, 5 g Texanol, 1.5 g BERMODOL PUR 2102 as a polyurethane thickener, 1 g biocide and 15 g control water were added to the slurry and mixed for 10 minutes at 1000 rpm with mechanical mixer.

In preparation of paint formulations, the synthesized different NaPAA polymers and NaP(AA-MA) copolymers were used as dispersing agent with constant amount. In Table 3.3 :, the synthesized different NaPAA polymers and NaP(AA-MA) copolymers was shown which used in the prepared paint formulation.

Table 3.3 : Synthesized different dispersing agent used in paint formulations.

Synthesized Dispersing Agent Code	Prepared Paint Formulation Code
S1	P1
S6	P6
S7	P7
S8	P8
S9	P9
S10	P10
S11	P11
C1	P12
C2	P13

3.6.2 Grindometer measurements of paint formulations

In order to determine fineness of dispersion and detection of oversize particles in paint dispersion, grindometer measurements of paint formulations were realized with Sheen brand Grindometer. The results of the grindometer measurements of paint formulations was obtained as micron scale and Hegmann gauge.

3.6.3 Hiding Power Test of paint formulations

The efficiency of milling and dispersion of pigments has important effect on opacity of the paint film. The hiding power of paint film reduces when pigments and extenders are not well dispersed. The paint films were applied to hiding power cards via four sided film applicator. In the next step, the luminous Y-reflectance the darker

and the lighter area of it were measured with a spectrophotometer for calculating opacity value of prepared paint formulations.

3.6.4 Gloss Measurements of paint formulations

In order to gloss measurements of paint formulations, 100-micron thickness paint films were applied to 10x15 cm standard glass substrates via four sided film applicator. Then 20°, 60° and 85° gloss were measured for specifiyng the appearance of paint films prepared with NaPAA and NaP(AA-MA) dispersing agents.

3.6.5 Viscosity measurements of paint formulations

The initial viscosity of paint formulations was measured using a low shear viscometer Brookfield Model DV-II with in order to determine dispersion and stabilization efficiency of synthesized NaPAA polymers and NaP(AA-MA) copolymers in paints. For each of measuring viscosity, after a few minutes of stirring of the paint formulations, the Brookfield viscosities of the different paint formulations were measured with spindle s-64 at 1 rpm at 20 °C.

3.6.6 Storage stability measurements of paint formulations

According to Standard Test Method for Package Stability of Paint, the storing the water borne paint for 1 month at 52±1°C simulates some of the effects of storage for 6 months to 1 year at 23±2°C. The rheological stability of the prepared paint formulations over time and under temperature was determined by measuring the Brookfield viscosities of the different paint formulations at 1 rpm with spindle s-64 at 20 °C, after storage one week for one month at 52±1 °C.

Firstly, the stored paint samples was bring to 20° C and noted any evidence of pressure or vacuum in the unopened container. When the container was opened, any skinning, corrosion, souring and odor of putrefaction were investigated. Then, the paint was stirred about 300 stirs in 2 minutes with a spatula appropriate to the container as to ensure uniform distribution of any settled material. The avoiding the use of a mechanical mixer was important due to it might disperse particles which it would not be dispersed by hand stirring. After stirring, the viscosity of the paint measured. The viscosity value of the stored paint sample should not be 15% less or more than the initial viscosity value of the paint sample.

4. RESULTS AND DISCUSSION

In this study, stabilization of water borne paint formulations was examined by using sodium salts of polyacrylic acid (NaPAA) and sodium salts of acrylic-maleic copolymers anhydride NaP(AA-MA) as a dispersant agent. PAA was synthesized from controlled radical polymerization of acrylic acid via reversible addition-fragmentation chain transfer (RAFT) method and P(AA-MA) was synthesized from controlled radical copolymerization of acrylic acid and maleic anhydride via same method. NaPAA and NaP(AA-MA) were obtained neutralization of PAA with sodium hydroxide (32% wt.).

In order to determine optimal polymerization parameters, NaPAA was synthesized in five different ways which were varying amount of chain regulator, sodium hypophosphite, (0 wt%, 0.05 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt%), ratio of initiator and monomer (ammonium persulfate/acrylic acid %: 2.5%, 5%, 6% and 7.5%), feeding time of monomer (4.5, 5.5 and 6.5 hours) and amount of solvent, isopropyl alcohol, (5 wt% and 10 wt%). In order to determine desirable acrylic acid-maleic anhydride monomers ratio, NaP(AA-MA) was synthesized in AA/MA: 1:1 and 1:0.5 ratio.

The synthesized samples were structurally identified by performing the FTIR characterization. The solid content of polymers was determined by rapid solid content analyzer. The Brookfield viscosity of polymers was measured at 6 rpm at 20°C. Molecular weight and molecular weight distribution were determined via GPC equipped tetra detection of RALS and LALS, RI, UV and viscometer detectors.

The viscosity of calcite slurries was measured using a low shear viscometer Brookfield Model DV-II at 60 rpm and 20 °C in order to determine dispersion efficiency of synthesized NaPAA polymers and NaP(AA-MA) copolymers.

The zeta potential of calcite suspensions added varying amount of NaPAA and NaP(AA-MA) as a dispersant was measured with zeta potential meter in order to examine stabilization of calcite slurries.

A sample formulation of water borne white plastic paint that has 74 PVC value was chosen in order to examine the performance of waterborne paint formulations. Water borne white plastic paint formulation were prepared with synthesized NaPAA polymers and NaP(AA-MA) copolymers as a dispersing agent.

The grindometer measurement of paint formulations was realized for confirming fineness of dispersion and detecting of oversize particles in paint dispersion.

The paint films were applied to hiding power cards. In the next step, the luminous Y-reflectance the darker and the lighter area of it were measured with a spectrophotometer for calculating opacity value of prepared paint formulations.

The initial viscosity of paint formulations was measured using a low shear viscometer Brookfield Model DV-II with in order to determine dispersion and stabilization efficiency of synthesized NaPAA polymers and NaP(AA-MA) copolymers in paints.

The rheological stability of the prepared paint formulations over time and under temperature was determined by measuring the Brookfield viscosities of the different paint formulations at 1 rpm with spindle s-64 at 20 °C, after storage one week for one month at 52±1 °C.

4.1 Dispersing Agent Samples Characterization

4.1.1 FTIR-ATR spectrophotometric analysis

The FTIR spectra of the PAA and NaPAA were presented in Figure 4.1 :and Figure 4.2 :. The FTIR spectra of the P(AA-MA) and NaP(AA-MA) were presented in Figure 4.3 : and Figure 4.4 :. FTIR spectra were recorded in the absorbance mode. The wave numbers of characteristic peaks is shown on the figures. These signals were helpful in identifying the components of the polymerization of PAA and neutralization of PAA with NaOH.

FTIR spectra of polyacrylic acid and the sodium salt polyacrylic acid are observed in the figure below. Since except C=C band all other bands are the same in both acrylic and polyacrylic acid. The strong two peaks of C=C band at 1617-1634 cm^{-1} distinguishes between acrylic and polyacrylic acid. Stretching group of C = O at 1701 cm^{-1}, asymmetrical stretching group of COO^- at 1542-1645 cm^{-1}, symmetric

stretch group of COO^- at about 1403 cm^{-1}, asymmetric stretch group of CH_2 at 1451 cm^{-1} and 1452 cm^{-1}, asymmetric stretch group of C-C-C at 1050 cm^{-1}, stretching group of C-O at 1150 cm^{-1} are shown in the following spectra.

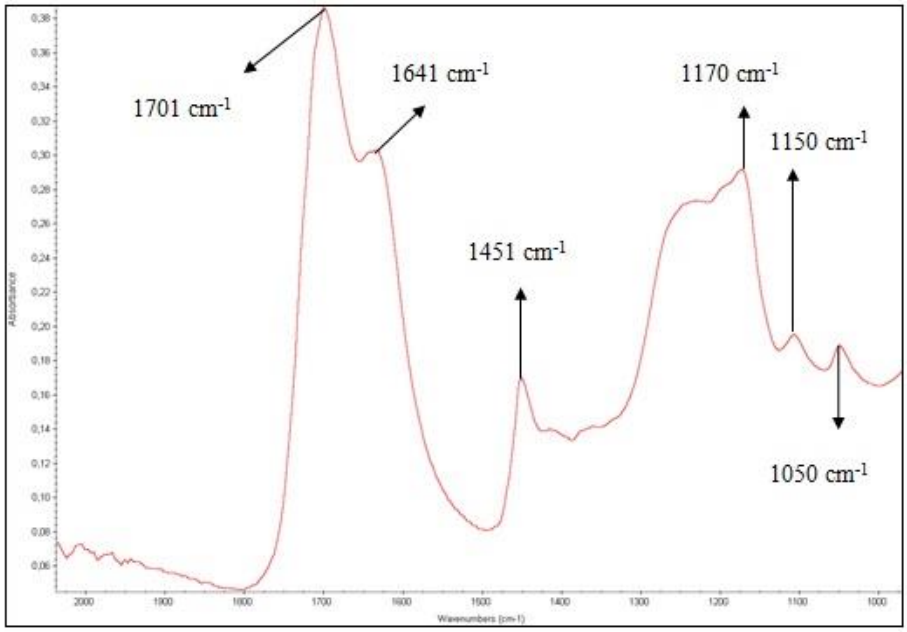


Figure 4.1 : FTIR analysis of PAA.

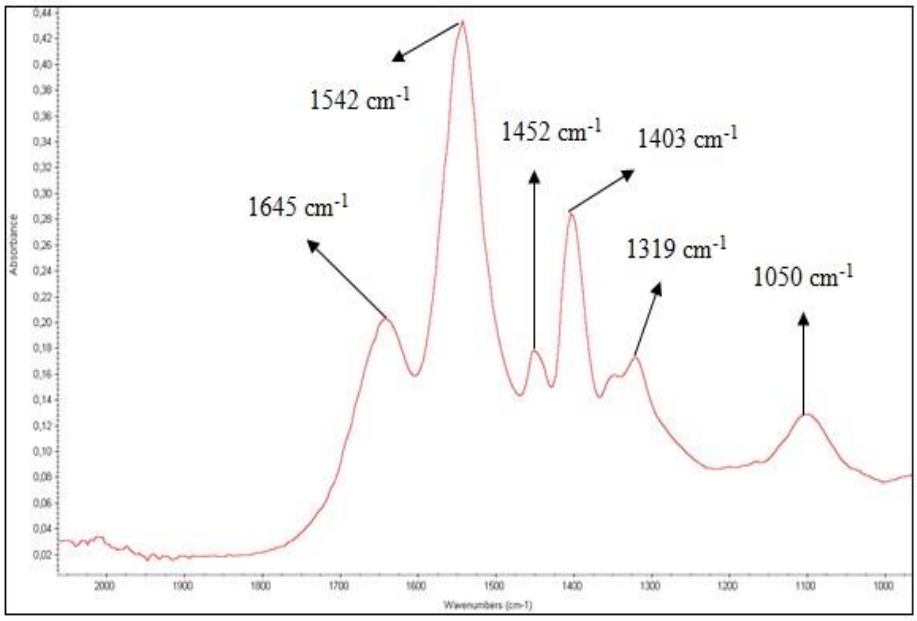


Figure 4.2 : FTIR analysis of NaPAA.

The FTIR spectrum of poly (acrylic acid-co-maleic anhydride) was shown in the figure below. Stretching group of O-H at 3358 and 3250 cm^{-1}, bending vibration group of C-H at 2971 cm^{-1} and 1395 cm^{-1}, the symmetric and asymmetric stretching

vibration of C = O groups at 1636 – 1630 cm^{-1} and 1550 cm^{-1} are shown in the following spectra. There was no absorption peaks at 1820 cm^{-1} ~ 1840 cm^{-1} of the anhydride groups and 665 cm^{-1} to 995 cm^{-1} of the C = C groups of maleic anhydride monomer in the synthesized polymer.

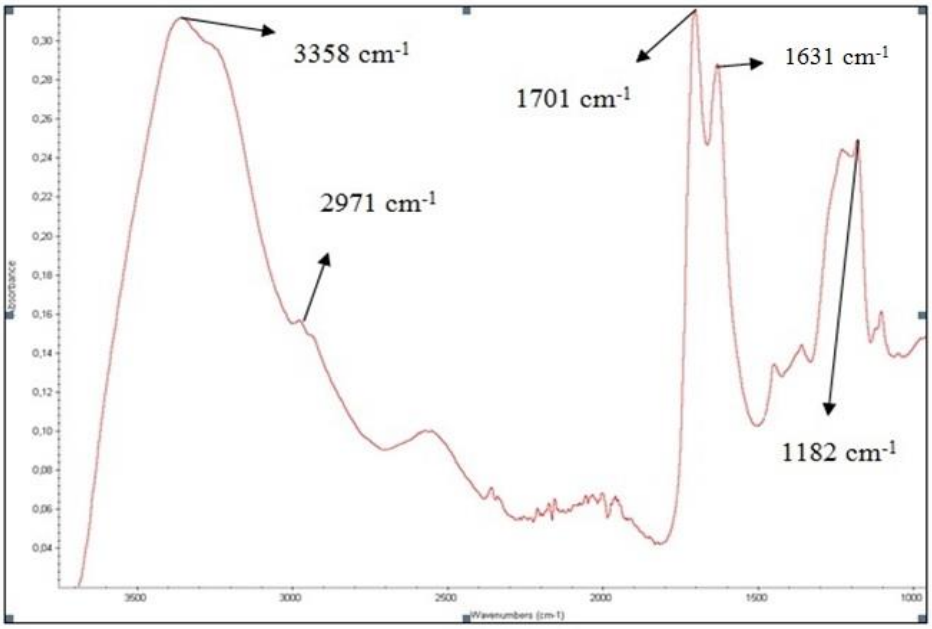


Figure 4.3 : FTIR analysis of P(AA-MA).

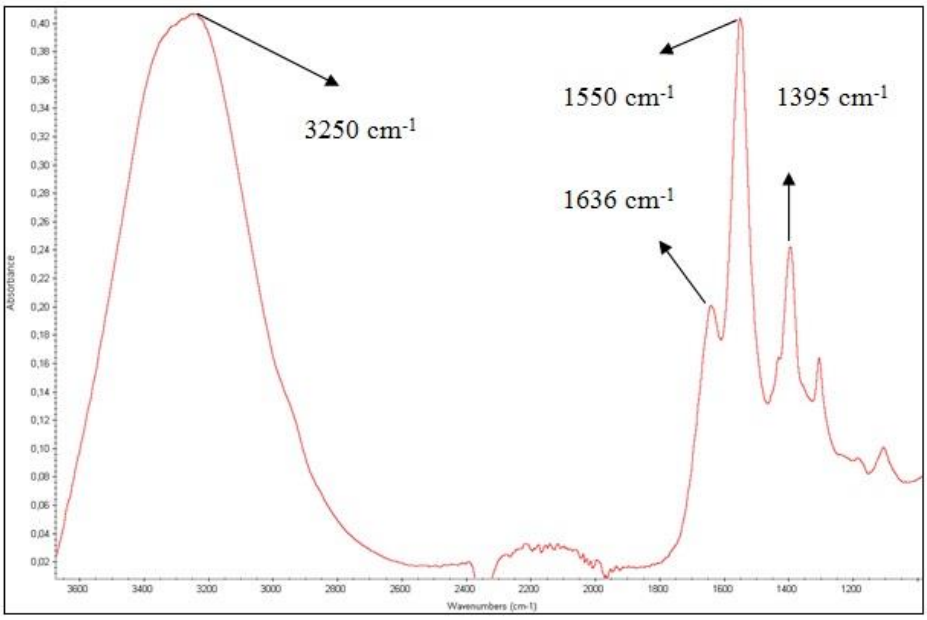


Figure 4.4 : FTIR analysis of NaP(AA-MA).

4.1.2 The solid content of synthesized and neutralized polymers and copolymers

Sartorius MA 35 is a rapid dryer and was used to determine the solid content of synthesized and neutralized polymers and copolymers during this study. The solid

content of synthesized all PAA, NaPAA, P(AA-MA) and NaP(AA-MA) was illustrated in Table 4.1 :.

4.1.3 The viscosity of synthesized and neutralized polymers and copolymers

Brookfield Model DV-II Viscometer at 60 rpm was used to measure the viscosity of polymer at the end of the polymerization and neutralization with NaOH at 20°C. The Brookfield viscosity of synthesized all PAA, NaPAA, P(AA-MA) and NaP(AA-MA) and also pH values were illustrated in Table 4.1 :.

4.1.4 GPC results

In order to determine the molecular weight and molecular distribution of synthesized PAA, P(AA-MA), NaPAA and NaP(AA-MA) Viskotek VE2001 GPC Max was used as follows tetra detection of RALS and LALS, RI, UV and viscometer detectors.

Firstly, in order to determine desirable amount of chain transfer regulator, sodium hypophosphite, NaPAA was synthesized in five different amount of sodium hypophosphite 0 wt%, 0.05 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt%. The results of molecular weight and molecular distribution of synthesized NaPAA were illustrated in Table 4.1 :.

Table 4.1 : Varied amount of sodium hypophosphite.

Samples	NaHyp (wt %)	Solid (wt %)	pH	Brookfield Viscosity at 20°C (Cp)	Mw, g/mol	Mn, g/mol	PDI	AA Conversion %
S1	0	51.12	1.12	986.7	20039	8642	2.319	87.04
S1_Na		41.10	7.49	875.8	20122	8838	2.277	-
S2	0.05	49.63	1.06	277.4	12117	6107	1.984	92.62
S2_Na		41.18	8.04	170.0	12226	6339	1.929	-
S3	0.10	50.60	1.04	439.2	9345	4220	2.214	93.06
S3_Na		40.14	7.37	216.5	9499	4428	2.145	-
S4	0.15	48.86	1.18	254.6	7104	4075	1.743	94.68
S4_Na		39.51	7.86	180.5	7223	4463	1.618	-
S5	0.20	49.24	1.33	293.9	7871	4399	1.789	96.59
S5_Na		39.69	7.22	200.5	7967	4766	1.672	-

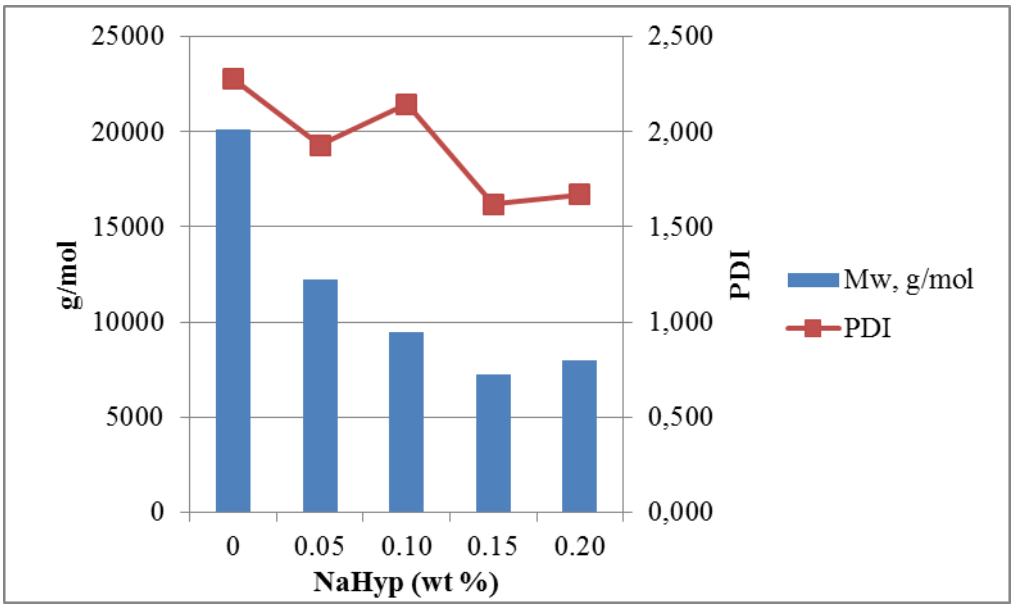


Figure 4.5 : Varied amount of NaHyp versus molecular weights and PDIs.

According to the results of molecular weight and molecular distribution of synthesized NaPAA in Figure 4.5 :, the desirable amount of chain transfer regulator, sodium hypophosphite for further reaction is 0.15 wt% by weight according to the total content of total reaction mixture.

Secondly, in order to determine suitable ratio of initiator and monomer (APS/AA %:), NaPAA was synthesized in four different ratio of initiator and monomer %: 2.5%, 5%, 6% and 7.5%. The results of molecular weight and molecular distribution of synthesized NaPAA were illustrated in Table 4.2 :.

Table 4.2 : Varied ratio of initiator and monomer.

Samples	APS/AA Ratio	Solid (wt %)	pH	Brookfield Viscosity Cp at 20°C	Mw, g/mol	Mn, g/mol	PDI	AA Conversion %
S6	2.5	50.59	1.07	2619.0	12802	8724	1.467	93.69
S6_Na		39.15	7.97	7548.0	14116	7448	1.895	-
S7	5	50.95	0.97	378.9	7075	4539	1.559	94.73
S7_Na		38.49	8.19	181.0	7886	4369	1.805	-
S8	6	51.71	0.95	369.4	5568	3545	1.571	94.60
S8_Na		39.05	8.22	143.0	6235	3640	1.713	-
S9	7.5	51.55	1.04	407.9	5492	3593	1.529	94.40
S9_Na		39.01	7.89	136.0	5803	3273	1.773	-

According to the results of molecular weight and molecular distribution of synthesized NaPAA in Figure 4.6 :, the lowest molecular weight poymer was obtained with 7.5% ratio of APS and AA but the lowest molecular distribution of polymer was obtained with 6% ratio of APS and AA monomer.

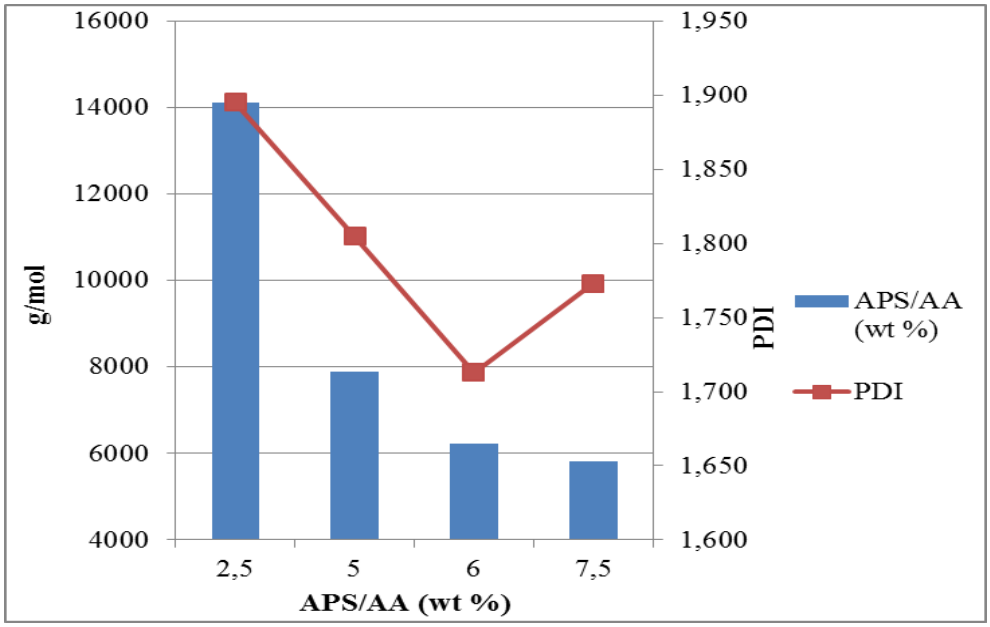


Figure 4.6 : The effects of the varied ratio of APS/AA on molecular weight and molecular distribution of NaPAAs.

Then, in order to examine effects of the feeding time of monomer and initiator on molecular weight and molecular distribution of PAA and NaPAA, it was synthesized in three different feeding time of AA and APS. The feeding time of AA was changed in 4.5, 5.5 and 6.5 hours. The feeding of APS was finished about 15 minute after finishing of AA feeding. The results of molecular weight and molecular distribution of synthesized NaPAA were illustrated in below table.

Table 4.3 : Varied feeding time of monomer and initiator.

Samples	Feeding Time	Solid (wt %)	pH	Brookfield Viscosity Cp at 20°C	Mw, g/mol	Mn, g/mol	PDI	AA Conversion %
S10	4.5	47.89	1.11	315.9	7051	4351	1.621	94.90
S10_Na		39.96	7.91	286.9	8437	4368	1.932	-
S8	5.5	51.71	0.95	369.4	5568	3545	1.571	94.60
S8_Na		39.05	8.22	243.0	6235	3640	1.713	-
S11	6.5	46.07	1.02	295.0	5543	3415	1.623	98.72
S11_Na		37.29	8.06	116.5	5893	3784	1.557	-

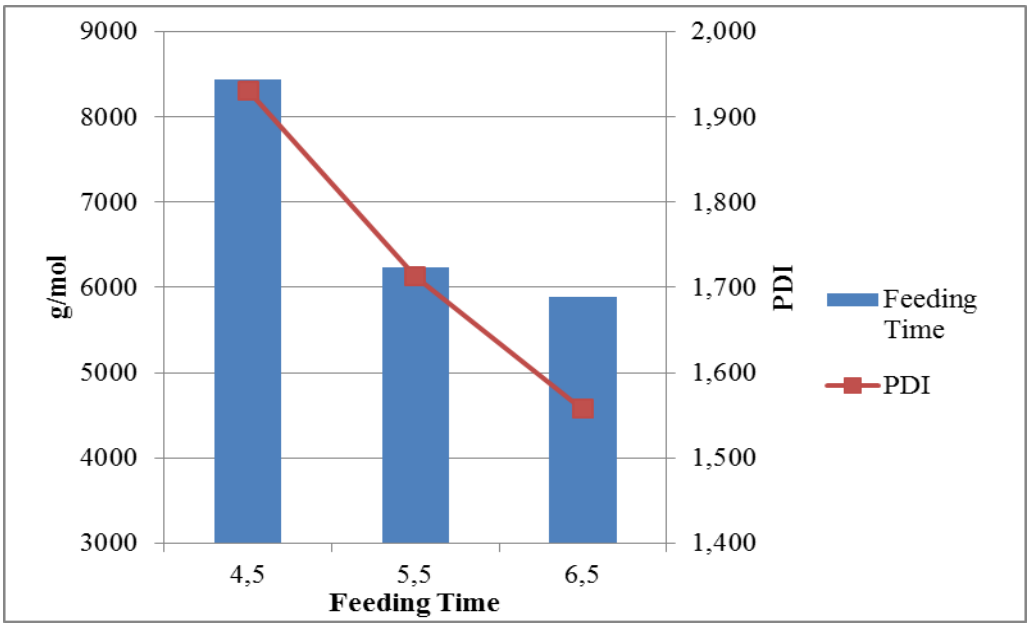


Figure 4.7 : The effects of the varied feeding time of monomer and initiator on molecular weight and PDI of NaPAAs.

According to the results of molecular weight and molecular distribution of synthesized NaPAA in Figure 4.7 :, the feeding time of monomer and initiator influences on molecular weight and narrow molecular weight distribution of NaPAA. When the feeding time was increased, molecular weight was decreased and molecular weight distribution was narrowed.

Furthermore, in order to invistigate effects of the different amount of solvent on molecular weight and molecular distribution of PAA and NaPAA, it was synthesized in two different amount of IPA. The amount of IPA was changed in 5 wt% and 10 wt% by weight percent according to total content of reaction mixture. The results of molecular weight and molecular distribution of synthesized NaPAA were illustrated in Table 4.4 :.

Table 4.4 : Varied amount of solvent.

Samples	IPA (wt %)	Solid (wt %)	pH	Brookfield Viscosity Cp at 20°C	Mw, g/mol	Mn, g/mol	PDI	AA Conversion %
S12	5	53.03	0.80	2859	9932	6283	1.581	87.40
S12_Na		41.77	7.55	527.9	14182	6303	2.250	-
S8	10	51.71	0.95	369.4	5568	3545	1.571	94.60
S8_Na		39.05	8.22	143.0	6235	3640	1.713	-

According to the results of molecular weight and molecular distribution of synthesized NaPAA in Figure 4.8 :, the suitable amount of solvent for polymerization of AA is 10% by weight percent according to total weight of reaction mixture. In addition, IPA was controlled the reaction temperature at 80°C and prevented extreme temperature rising during exothermic acrylic acid polymerization.

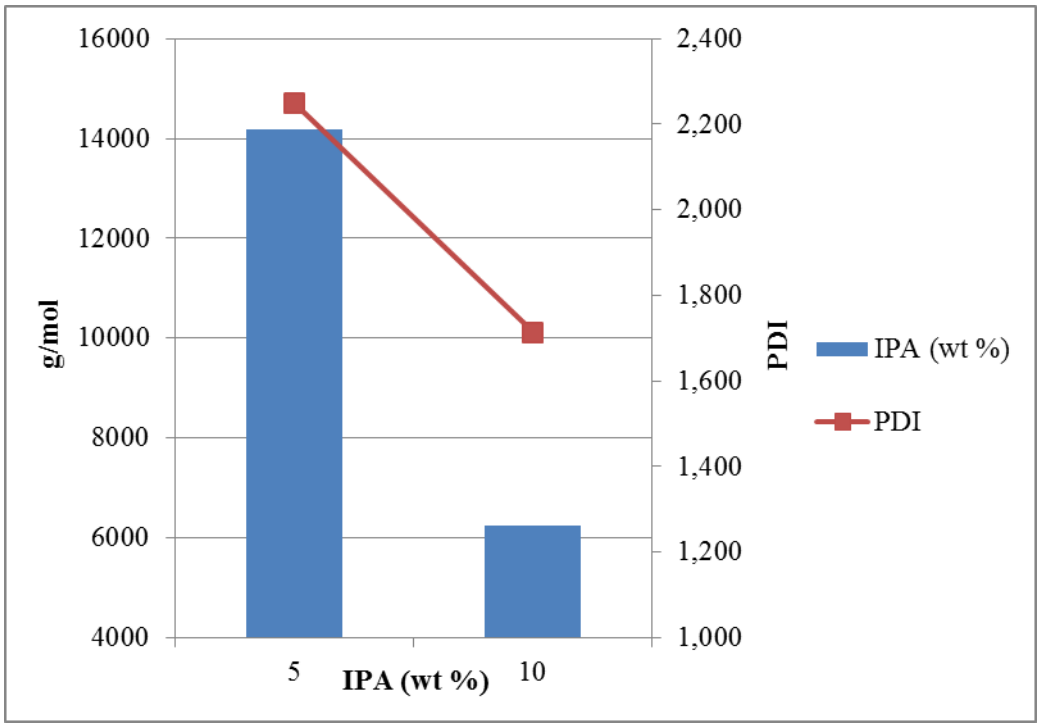


Figure 4.8 : The effects of the amount of IPA on molecular weight and PDI.

In order to determine desirable acrylic acid-maleic anhydride monomers ratio, NaP(AA-MA) was copolymerized in AA/MA: 1:1 and 1:0.5 ratio.

Table 4.5 : Varied ratio of acrylic acid-maleic anhydride monomers.

Samples	AA/MA Monomer ratio	Solid (wt %)	pH	Brookfield Viscosity Cp at 20°C	Mw, g/mol	Mn, g/mol	PDI
C1	1:0.5	46.59	3.30	332.9	10347	4516	2.291
C1_Na		36.85	7.69	170.5	10632	5135	2.070
C2	1:1	48.18	0.56	191.0	10320	5058	2.040
C2_Na		36.83	7.93	91.0	11528	5096	2.262

According to the results of molecular weight and molecular distribution of synthesized NaP(AA-MA) in Figure 4.9 :, lower molecular weight and molecular distribution were obtained in AA/MA: 1:1 monomers ratio.

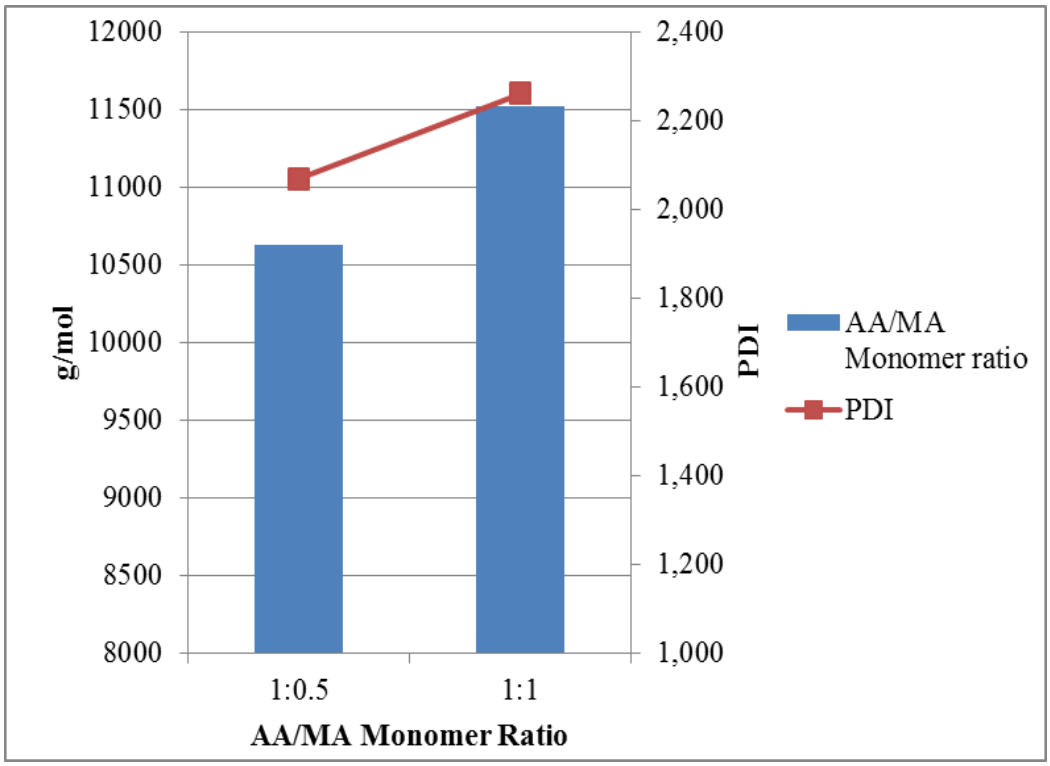


Figure 4.9 : The effects of the varied ratio of AA/MA on molecular weight and PDI.

4.1.5 The Brookfield viscosity calcite dispersions

The comparison of the Brookfield viscosity of calcite slurries prepared NaPAA was shown in Figure 4.10 :, in order to determine dispersion efficiency of synthesized NaPAA polymers. According to this curve of viscosity, prepared calcite slurries of S1_Na was the highest viscosity than the others calcite slurries. In addition, the molecular weight of S1_Na was 20122 g/mol and its PDI value was 2.277 and very broadly.

According to Figure 4.11 : of the viscosity of dispersions versus NaPAA dispersant agents concentration, prepared calcite slurries that used S7_Na, S8_Na and S9_Na were lower viscosity than the others calcite slurries. In addition, S8_Na's calcite slurry has the lowest viscosity value at 0.02% and 0.03% of usage percent according the total weight of calcite in dispersion. The molecular weight of S8_Na was 6235 g/mol and its PDI value was 1.713.

Also, the comparison of the Brookfield viscosity of calcite slurries prepared NaP(AA-MA) copolymers was shown in below graph table in order to determine dispersion efficiency of synthesized different monomer ratio of NaP(AA-MA) copolymers.

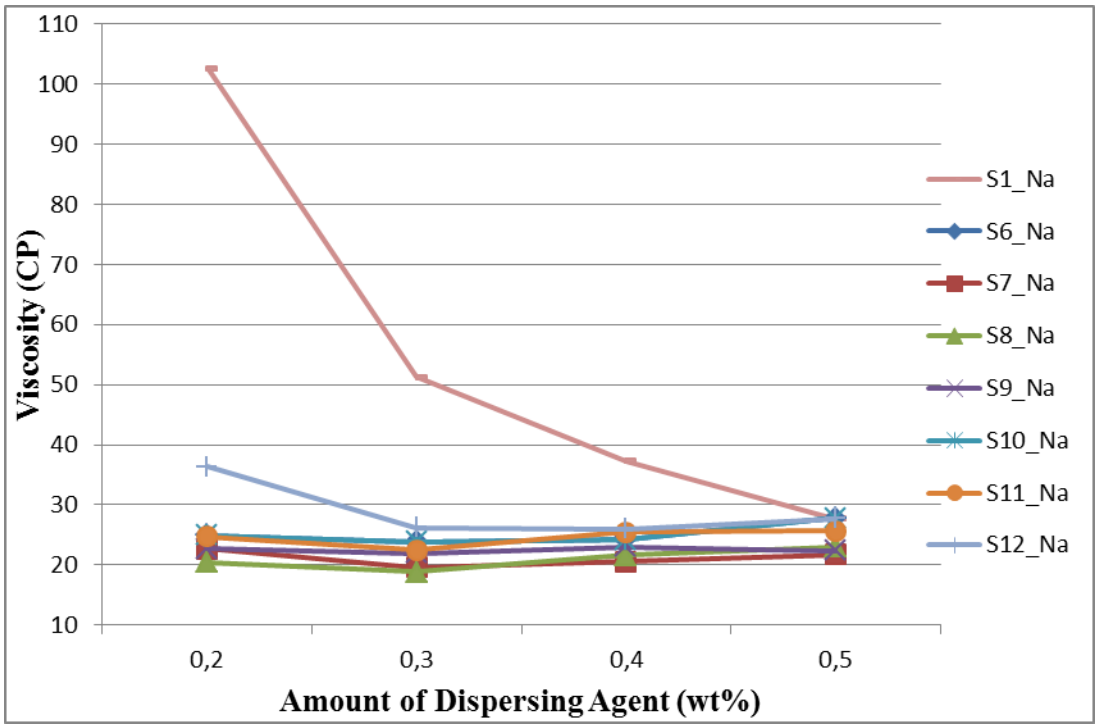


Figure 4.10 : The comparison of the viscosity of calcite dispersions with NaPAA.

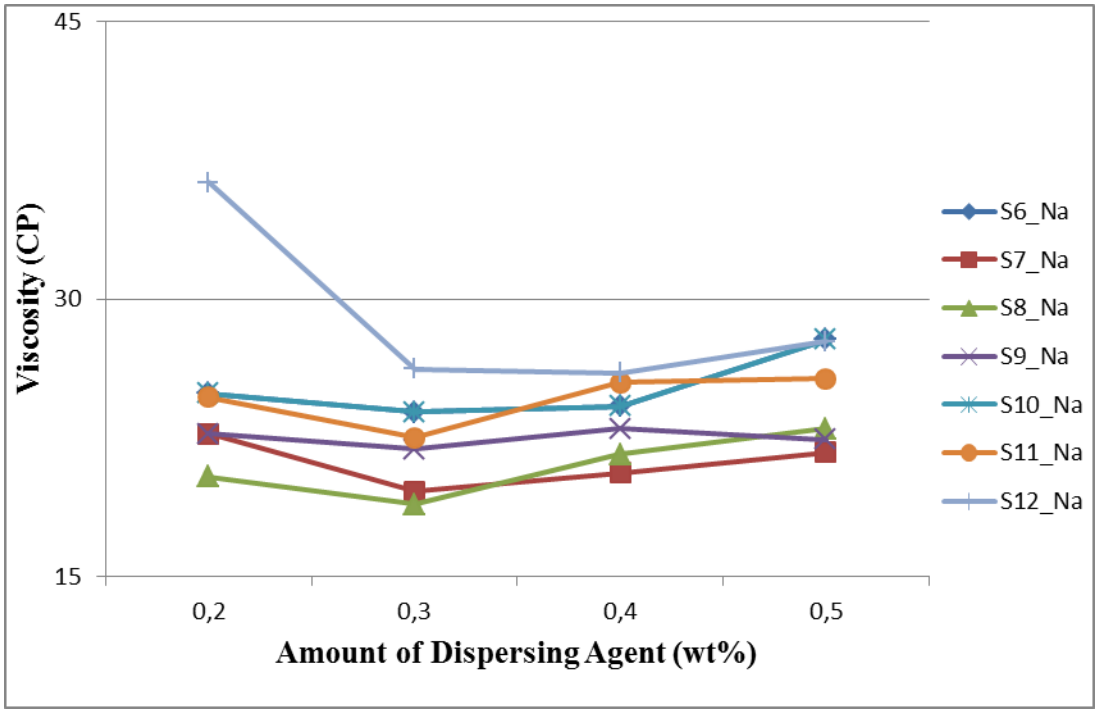


Figure 4.11 : The comparison of the viscosity of calcite dispersions except S1_Na.

According to the graph in Figure 4.12 : of the viscosity of dispersions versus NaP(AA-MA) dispersant agents concentration, the prepared calcite slurries added C1_Na was lower viscosity than C2_Na. The molecular weight of C1_Na was 10632 g/mol and its PDI value was 2.070. There was a significant difference of PDI values,

so C1_Na that was synthesized 1:0.5 AA/MA monomer ratio showed better dispersing efficiency than C2_Na.

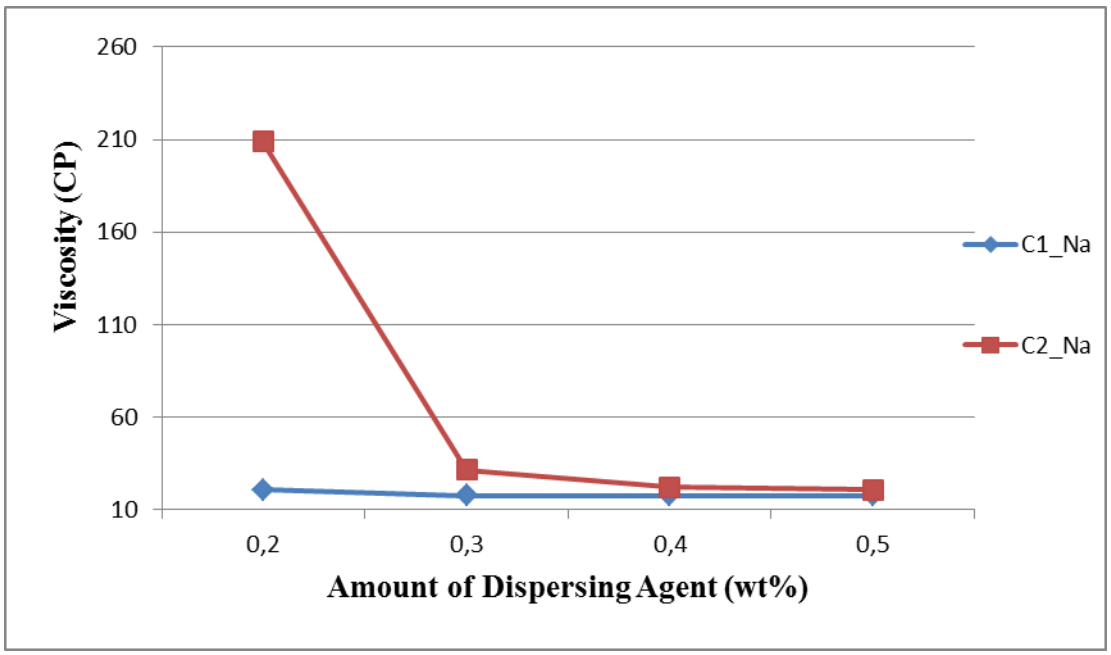


Figure 4.12 : The comparison of the viscosity of dispersions NaP(AA-MA).

Moreover, when the viscosity of calcite dispersions of NaPAA polymers and NaP(AA-MA) copolymers compared in Figure 4.13 :, C1_Na copolymer produced the better dispersion performance than NaPAA polymers.

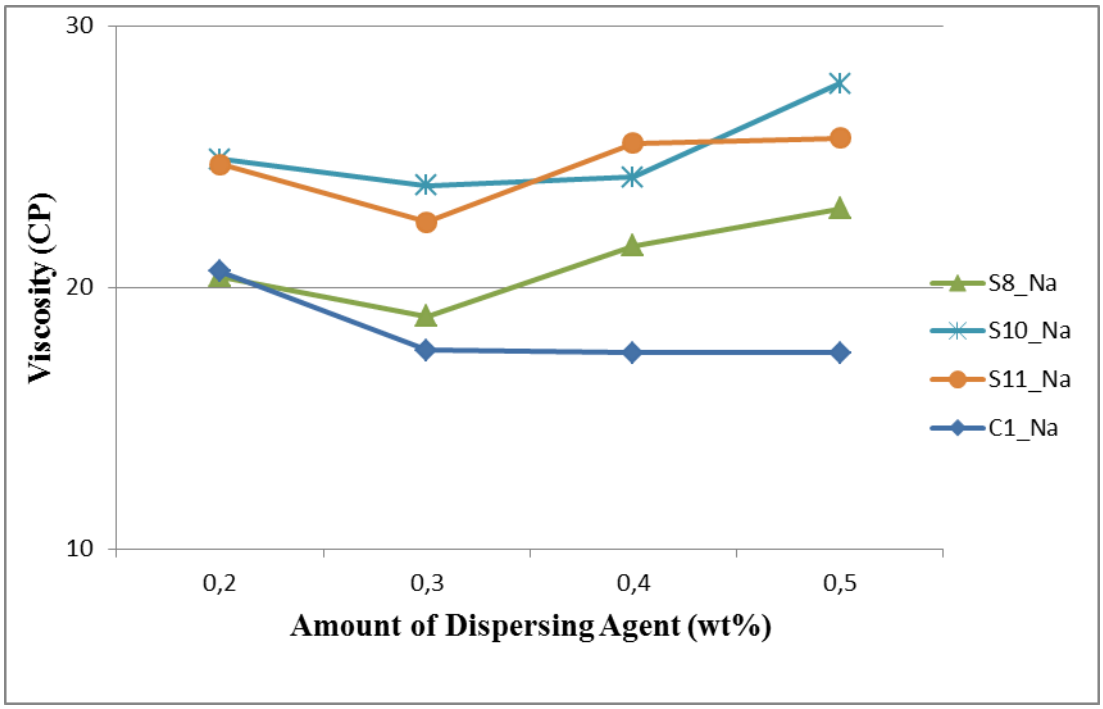


Figure 4.13 : The viscosity of dispersions NaPAA versus NaP(AA-MA).

4.1.6 The zeta potential of calcite dispersions

The results of the zeta potential of calcite dispersions added varying amount of NaPAA polymers was measured with zeta potential meter in order to examine stabilization of calcite slurries.

According to the graph of the zeta potential of dispersions versus NaPAA dispersant agents concentration, the prepared calcite slurries added S8_Na and S11_Na were lower viscosity than others at 0.05% of usage percent according the total weight of calcite in dispersion. However, S11_Na has slightly lower zeta potential than S8_Na zeta potential value. When S8_Na was synthesized, sodium hypophosphite was added as 0.15 weight percent of according to the total amount of reaction mixture and IPA was added 10% weight percent of reaction mixture and feeding time of monomer was 5.5 hours. The difference polymerization condition of S11_Na was the feeding time of monomer 6.5 hours so it has narrow PDI according to S8_Na's PDI value.

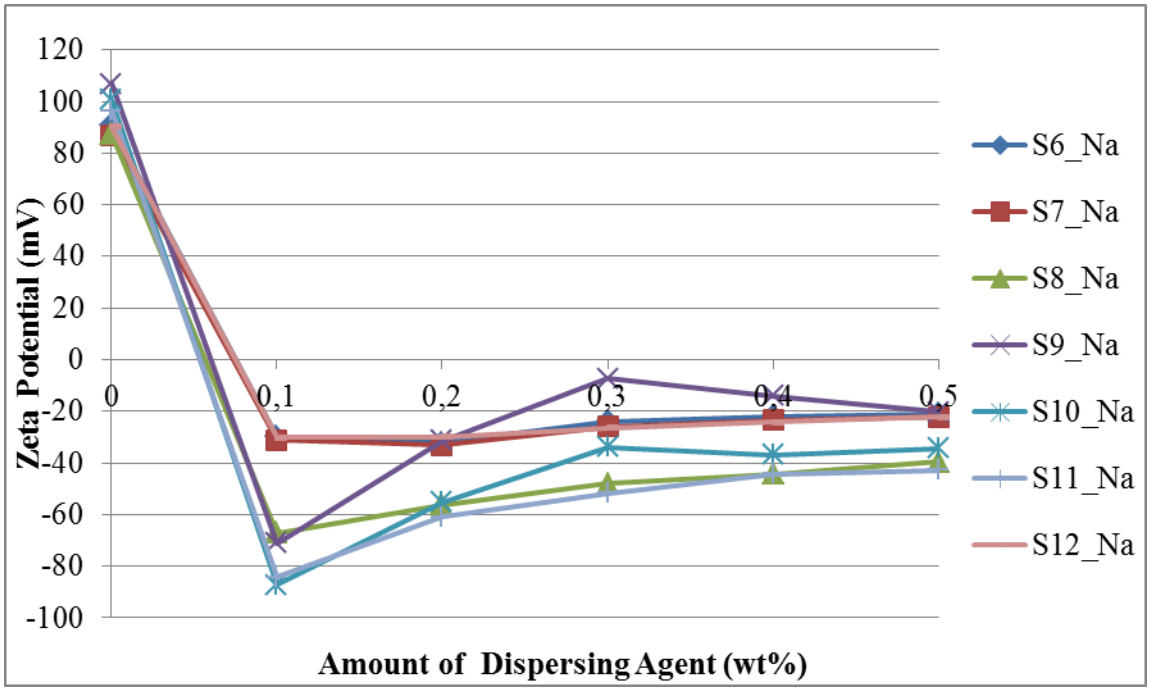


Figure 4.14 : The comparison of the zeta potential of calcite dispersions NaPAA.

In addition, the comparison of the zeta potential value of calcite dispersions added varying amount of NaPAA polymers and NaP(AA-MA) copolymers was shown in Figure 4.15 :. C1_Na has the lowest zeta potential result than other polymers and copolymer of C2_Na viscosity different from the results of viscosity of calcite dispersions.

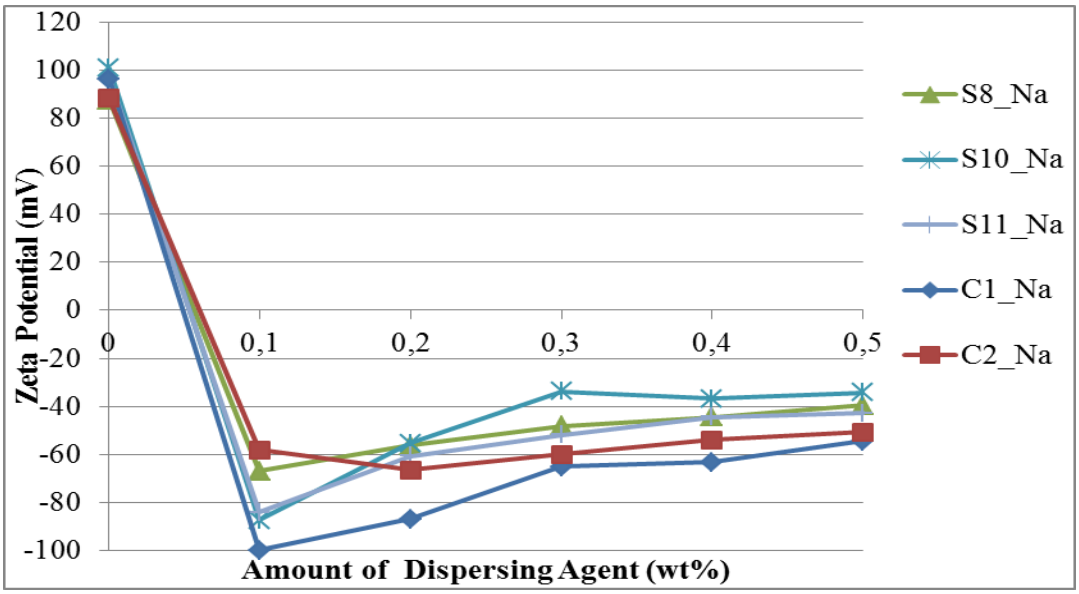


Figure 4.15 : The zeta potential of dispersions NaPAA versus NaP(AA-MA).

4.1.7 NMR results

In order to determine copolymer conversion, ^{1}H-NMR studies were carried out with deuterated water as a solvent. C1_Na and C2_Na samples were dried in microwave oven and then prepared for NMR sampling. The ^{1}H-NMR spectrum of the C1_Na copolymer that was synthesized in 1:0.5 AA/MA monomer ratio was shown in Figure 4.16.

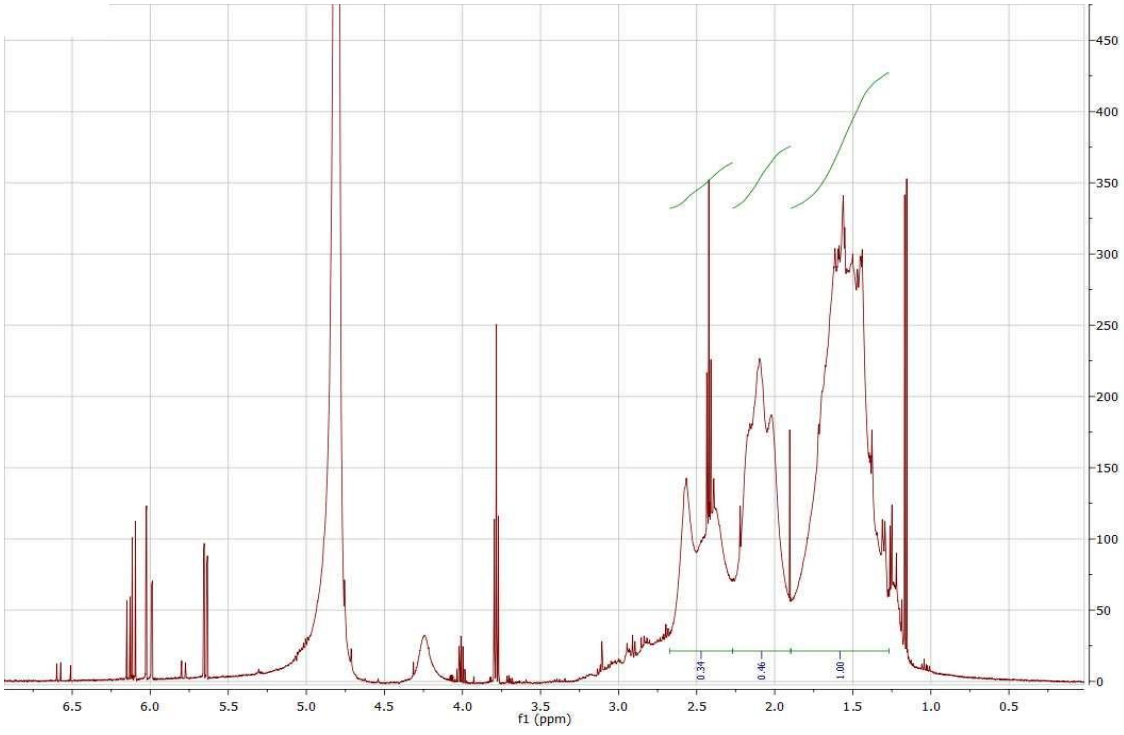


Figure 4.16 : The 1H-NMR spectrum of the C1_Na copolymer.

The spectrum displayed characteristic peaks at δ=1.27-1.90 ppm (CH_2 groups) and δ=1.91-2.27 ppm (CH groups) which were related to acrylic acid units, and δ=2.29-2.67 ppm (CH groups) which was related to maleic anhydride units. In addition, deuterated water given at δ=4.8 ppm. The integral area of CH_2 groups was 1 unit, so protons coming from the CH_2 was 0.50 unit. The total integral area of CH groups which were related to acrylic acid and maleic anhydride 0.80 unit. The two protons coming from the CH groups of maleic anhydride was 0.30 unit which was the differance of the total integral area of CH groups and integral area of CH_2 groups. According to these results, the monomer ratio of maleic anhydride was 23% and acrylic acid was 77%. However, theoretical monomer ratio of maleic anhydride was 33%.

The ^{1}H-NMR spectrum of the C2_Na copolymer that was synthesized in 1:1 AA/MA monomer ratio was shown in Figure 4.17.

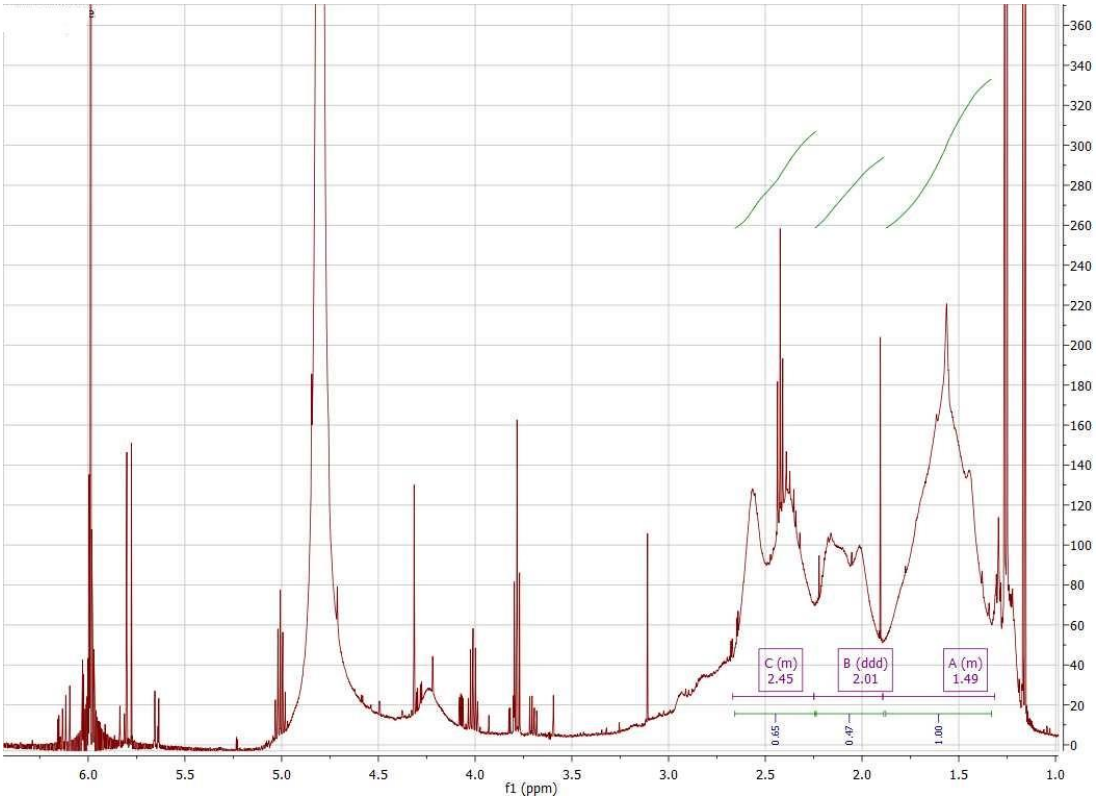


Figure 4.17 : The ^{1}H-NMR spectrum of the C2_Na copolymer.

The spectrum displayed characteristic peaks at δ=1.27-1.90 ppm (CH_2 groups) and δ=1.91-2.27 ppm (CH groups) which were related to acrylic acid units, and δ=2.29-2.67 ppm (CH groups) which was related to maleic anhydride units. In addition, deuterated water given peak at δ=4.8 ppm and unreacted acrylic acid CH and CH_2

protons given peaks at δ=5.78-6.18 ppm. The integral area of CH_2 groups was 1 unit, so protons coming from the CH_2 was 0.50 unit. The total integral area of CH groups which were related to acrylic acid and maleic anhydride 1.12 unit. The two protons coming from the CH groups of maleic anhydride was 0.62 unit which was the differance of the total integral area of CH groups and integral area of CH_2 groups. According to these results, the monomer ratio of maleic anhydride was 38% and acrylic acid was 62%. However, theoretical monomer ratio of maleic anhydride was 50%. The reason of this issue is steric inhibition. Maleic anhydride exhibits little tendency to copolymerization in water. In propagating step of copolymerization, the propagating radical to a monomer molecule is sterically hindered. So, the propagating step of copolymerization is exceedingly slow [50].

4.2 The Performance Test of Waterborne Paint Formulations

4.2.1 The grindometer measurements of paint formulations

The results of the grindometer measurements of prepared paint formulations was obtained as micron scale and Hegmann gauge. It is important for determining fineness of dispersion and detection of oversize particles in paint dispersion.

The fineness of dispersion was well obtained, when the grindometer result was small in micron scale and Hegmann Gauge. The results of the grindometer measurements is shown in Table 4.6 :. The fineness of dispersion of the prepared paint formulations P7, P8 and P12 have better than other paint formulations.

4.2.2 Hiding power test of paint formulations

The luminous Y-reflectance the darker and the lighter area of it were measured with a spectrophotometer for calculating opacity value of prepared paint formulations. The opacities of prepared paints was shown in below table. According to these results, P8 and P12 have better hiding power properties than other paint formulations. It was indicated that their pigments and extenders were well dispersed in paint formulations.

4.2.3 Gloss measurements of paint formulations

The 85° gloss result were illustrated in Table 4.6 :for specifiyng the appearance of paint films prepared with NaPAA and NaP(AA-MA) dispersing agents. According to

gloss measurements, prepared water borne white plastic paint formulations were matte paint due to the gloss value of them smaller than 5 gloss value.

Table 4.6 : The results of grindometer, opacity and gloss measurements.

Prepared Paint Formulation Code	Grindometer Measurements		Opacity	85° Gloss
	Micron	Hegmann Gauge		
P1	35	7	97.15	2.7
P6	30	7	97.49	2.9
P7	20	6	98.57	3.0
P8	20	6	99.14	3.4
P9	25	6-7	98.27	2.9
P10	25	6	97.98	2.9
P11	25	6-7	98.61	3.2
P12	20	6-7	99.19	3.9
P13	25	6	98.56	3.3

4.2.4 Storage stability measurements of paint formulations

According to Standard Test Method for Package Stability of Paint, the storing the water borne paint for 1 month at 52±1°C simulates some of the effects of storage for 6 months to 1 year at 23±2°C. The rheological stability of the prepared paint formulations over time and under temperature was determined by measuring the Brookfield viscosities of the different paint formulations at 1 rpm with spindle s-64 at 20 °C, after storage one week for one month at 52±1 °C.

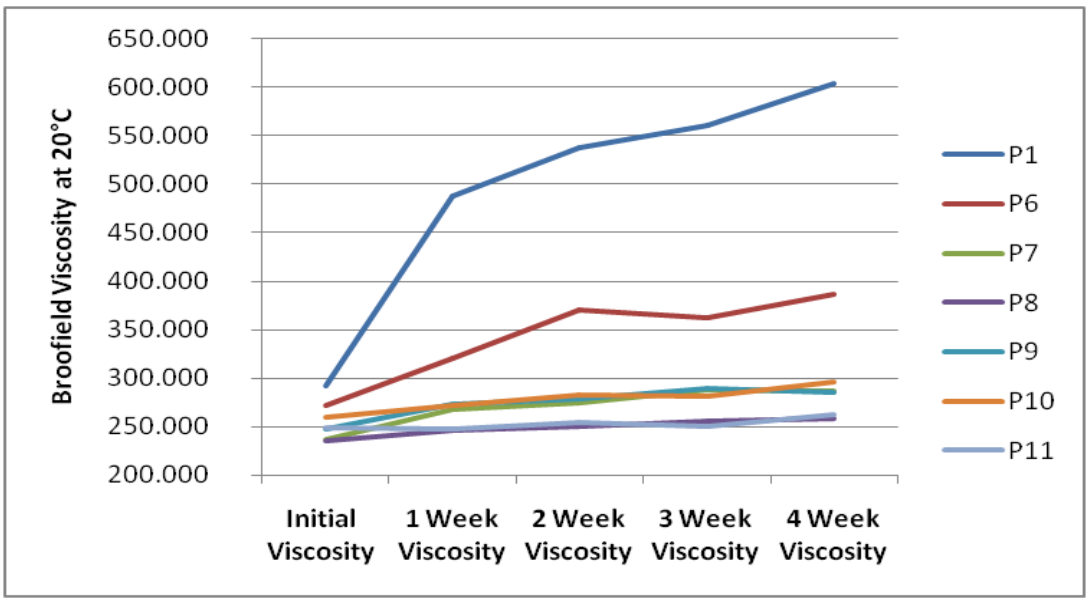


Figure 4.18 : The storage stability measurements of prepared paint formulations.

The storage stability measurements of prepared paint formulations was shown in Figure 4.19. According to this curve, P1 did not indicate rheological stability after storage for one month at 52±1 °C. On the other hand, P8 and P11 indicated best storage stability in NaPAA dispersants for one month at 52±1 °C according to Figure 4.19.

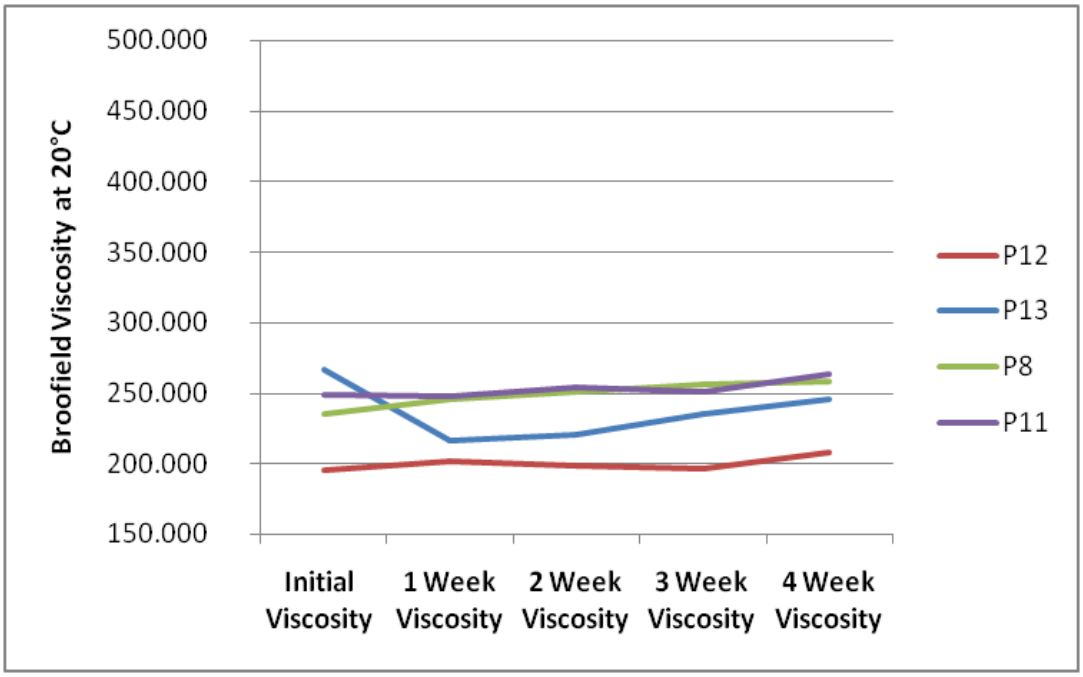


Figure 4.19 : The comparison of storage stability measurements.

5. CONCLUSION

The objective of this thesis was to examine stabilization of water borne paint formulations via adding sodium salts of polyacrylic acid (NaPAA) and sodium salts of copolymers of acrylic-maleic anhydride NaP(AA-MA) as a dispersant agent.

PAA was synthesized from controlled radical polymerization of acrylic acid via reversible addition-fragmentation chain transfer (RAFT) method and P(AA-MA) was synthesized from controlled radical copolymerization of acrylic acid and maleic anhydride via same method. NaPAA and NaP(AA-MA) were obtained from neutralization of PAA and P(AA-MA) with sodium hydroxide (32% wt.).

NaPAA was synthesized in five different ways which were varying amount of chain regulator, sodium hypophosphite, (0 wt%, 0.05 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt%), ratio of initiator and monomer (ammonium persulfate/acrylic acid %: 2.5%, 5%, 6% and 7.5%), feeding time of monomer (4.5, 5.5 and 6.5 hours) and amount of solvent, isopropyl alcohol, (5 wt% and 10 wt%).

In order to determine desirable acrylic acid-maleic anhydride monomers ratio, NaP(AA-MA) was synthesized in AA/MA: 1:1 and 1:0.5 ratios. The feeding time of acrylic acid was 6 hours, the weight percent of ammonium persulfate to total monomer content was 5%, the amount of sodium hypophosphite was 0.15% weight percentage according to the total weight of reaction mixture and the weight percent of isopropyl alcohol was 10% during the copolymerization of acrylic acid-maleic anhydride.

According to ^{1}H-NMR results of synthesized NaP(AA-MA) in AA/MA: 1:0.5 ratio, the monomer ratio of maleic anhydride was 23% and acrylic acid was 77%. However, theoretical monomer ratio of maleic anhydride was 33%.

According to ^{1}H-NMR results of synthesized NaP(AA-MA) in AA/MA: 1:1 ratio, the monomer ratio of maleic anhydride was 38% and acrylic acid was 62%. However, theoretical monomer ratio of maleic anhydride was 50%. The reason of this issue is steric inhibition. Maleic anhydride exhibits little tendency to

copolymerization in water. In propagating step of copolymerization, the propagating radical to a monomer molecule is sterically hindered. So, the propagating step of copolymerization is exceedingly slow towards maleic anhydride monomer. Furthermore, the (electrophilic) carboxylic group of acrylic acid stabilizes radicals and increases the affinity of radicals for acrylic acid monomer. Thus, radical groups on acrylic acid is more favorable than radical on maleic anhydride. This phenomena explains why the ratio of acrylic acid to maleic anhydride in the copolymer chain turns out to be higher compared to the ratio in the feed.

The synthesized samples were structurally identified by performing the FTIR characterization. FTIR spectrum gives the peaks that are expected due to the chemical structure of PAA, NaPAA, P(AA-MA) and Na(AA-MA). There was no absorption peaks at 1617~1634 cm^{-1} of C=C band acrylic acid in synthesized PAA and NaPAA polymers. Also, there was no absorption peaks at 1820 cm^{-1}~1840cm^{-1} of the anhydride groups and 665 cm^{-1} to 995cm^{-1} of the C = C groups of maleic anhydride monomer in the synthesized P(AA-MA) and NaP(AA-MA) copolymers.

In order to determine the molecular weight and the molecular distribution of synthesized polymers and copolymers were determined via GPC equipped tetra detection of RALS and LALS, RI, UV and viscometer detectors.

The viscosity of calcite slurries was measured using a low shear viscometer Brookfield Model DV-II at 60 rpm and 20 °C in order to determine dispersion efficiency of synthesized NaPAA polymers and NaP(AA-MA) copolymers when added different amounts. According to viscosity measurements of dispersions, prepared calcite slurries that added S8_Na has the lowest viscosity value at 0.02% and 0.03% of usage percent according the total weight of calcite in dispersion. The molecular weight of S8_Na was slightly higher than S9_Na but its PDI value was the lowest with 1.713.

According to the measurements of the viscosity of dispersions, the prepared calcite slurries added C1_Na was lower viscosity than C2_Na. The molecular weight of C1_Na was 10632 g/mol and its PDI value was 2.070. There was a significant difference of PDI values, so C1_Na that was synthesized 1:0.5 AA/MA monomer ratio showed better dispersing efficiency than C2_Na.

The zeta potential of calcite suspensions added varying amount of NaPAA and NaP(AA-MA) as a dispersant was measured with zeta potential meter in order to examine stabilization of calcite slurries. According to the results of the zeta potential of dispersions, the prepared calcite slurries added S11_Na, which has narrowest PDI, were lowest viscosity value than others at 0.05% of usage percent according the total weight of calcite in dispersion. However, when the molecular distribution of polymeric dispersant agent decreased, the dispersion efficiency of calcite slurry improved according to zeta potential of calcite suspensions.

Furthermore, when the viscosity of calcite dispersions of NaPAA polymers and NaP(AA-MA) copolymers compared, NaP(AA-MA) copolymer which synthesized 1:0.5 AA/MA monomer ratio produced the better dispersion performance than NaPAA polymers.

In order to examine the performance of waterborne paint formulations, a sample formulation of water borne white plastic paint that has 74 PVC value was chosen. Water borne white plastic paint formulation were prepared with synthesized NaPAA polymers and NaP(AA-MA) copolymers as a dispersing agent at 0.6% of usage percent according the total weight of formulations.

In order to determined fineness of dispersion and detection of oversize particles in paint dispersion, grindometer used with a scraper. It was stated that the fineness of dispersion of the prepared paint formulations P7, P8 and P12 have better than other paint formulations.

According to results of the hiding power test, P8 and P12 have better hiding power properties than other paint formulations. It was indicated that their pigments and extenders were well dispersed in paint formulations.

According to gloss measurements, prepared water borne white plastic paint formulations were matte paint due to the gloss value of them smaller than 5 gloss value. Additionally, the results of gloss measurements were similar to grindometer and hiding power test results. Therefore, P8 and P12 have higher 85° gloss value than other paint formulations.

The rheological stability changes of the prepared paint formulations over time and under temperature was determined by measuring the Brookfield viscosities of the different paint formulations at 1 rpm with spindle s-64 at 20 °C, after storage one

week for one month at 52±1 °C. According to these viscosities of the stored paint formulations, the P1, which was prepared with highest molecular weight and broadest molecular distributions NaPAA as a dispersing agent, was not rheological stability after storage one month at 52±1 °C. On the other hand, P8 and P11 indicated best storage stability in NaPAA dispersants.

In conclusion, the dispersion efficiency of it on calcite slurry improved when molecular weight and molecular distribution of polymeric dispersant agent decreased. In order to easily obtain low molecular weight and narrow molecular weight distribution NaPAA, sodium hypophosphite can be used as chain regulator in isopropyl alcohol and water media. In addition, the feeding time of monomer and initiator influences on molecular weight and narrow molecular weight distribution of NaPAA. When the feeding time was increased, molecular weight was decreased and molecular weight distribution was narrowed. Moreover, NaP(AA-MA) that was synthesized in 1:0.5 AA/MA monomer ratio can be used as dispersing agent in water borne paint formulations, instead of NaPAA polymers to present good storage stability performance in paints.

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